

INTERACTION OF MAGNESIUM ALLOYS WITH HYDROGEN

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Abstract

Interaction with hydrogen of intermetallics, solid solutions and multi-phase alloys in systems Mg-Ln (Ln = La, Ce, Er, Yb), Mg-Ca-M (M = Al, Zn, Ce, Cu, Ni), Mg-Ln-M (Ln = La, Ce, Sc, Y, Mn; M = Al, Ni) was investigated. The dependence of hydriding parameters of alloys on their phase composition and microstructure was established. On the basis of kinetic measurements the values of activation energy of hydriding-dehydriding in multi-component Mg-base systems was calculated and a model for reaction of Mg hydride formation in presence of rare-earth metals was proposed. The stability of hydrogen adsorption in pure and commercial hydrogen atmosphere was studied.

1. INTRODUCTION

A great deal of consideration has been given to interaction with hydrogen of some intermetallic compounds and magnesium alloys. This is mainly due to the fact that these compounds seem to be promising for preparing high-temperature hydrogen storage.

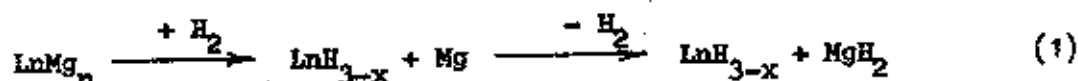
This paper summarizes the results of studying the interaction with hydrogen of magnesium alloys containing rare-earth metals and calcium. The results were obtained at the chair of high-pressure chemistry and physics of the Chemistry Department of Moscow State University. These metals have been chosen as the components of alloys because they actively interact with hydrogen and produce with magnesium the intermetallic compounds of various composition.

2. INTERACTION WITH HYDROGEN OF BINARY MAGNESIUM ALLOYS CONTAINING RARE-EARTH METALS

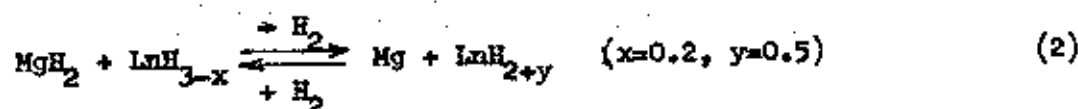
Hydriding of magnesium-rare-earth alloys was studied for intermetallics CeMg_{12} , $\text{Ce}_2\text{Mg}_{17}$, $\text{La}_2\text{Mg}_{17}$, $\text{Ce}_5\text{Mg}_{41}$, LaMg_3 and CeMg_2 , two-phase alloys containing these compounds, and for a solid solution of erbium in magnesium (15 wt. % of erbium) [1-5].

First hydration of alloys with lanthanum and cerium whose solubility in magnesium is low (about $10^{-2}\%$) leads to irreversible decomposition of intermetallics present in the alloys. At 600 K and 3 MPa the acicular crystals of lanthanide hydride $0.5 \times 0.5 \mu\text{m}$ in size are produced in the grains of intermetallic compounds (Fig. 1) with a simultaneous formation of the magnesium phase. An increase of the duration of exposure in hydrogen leads to hydriding of magnesium to MgH_2 .

The data reported in [6] and the experimental results indicate unambiguously that the interaction with hydrogen of intermetallic compounds of the magnesium-rare-earths type is described by Equation (1)



The use of two-phase compositions in as a working component hydrogen storage is based on the reaction described by Equation (2)

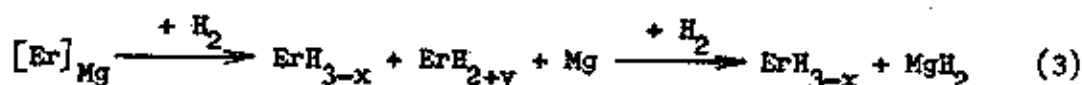


Magnesium formed in a mixture with hydride of rare-earth metals according to Equations (1,2) is highly reactive and interacts with hydrogen at a rate much exceeding the rate of interaction of individual magnesium.

Hydrogenolysis (1) takes place within a thin surface layer of about $10 \mu\text{m}$ in which, in the course of hydriding, cracks and peels off. The layer-by-layer metallographic and X-ray phase analyses indicate that the reaction extends deep into the sample along the grain boundaries of the intermetallic compounds, while for two-phase alloys the reaction goes over the inclusions of lanthanide-rich phases. These inclusions serve also to initiate hydriding of less active phase constituents. In pre-eutectic alloys hydriding proceeds successively from intermetallic phase inclusions to most highly dispersed

grains of magnesium and then to the large magnesium crystals of primary crystallization (Fig. 2).

The interaction with hydrogen of magnesium-based erbium-rich solid solution leads to a decomposition even at 550 K and is accompanied by the release of a two-phase mixture of erbium dihydride and erbium trihydride along the boundaries of the equiaxed magnesium crystallites 0.5–3 μm in size (Fig. 3). An increase in hydriding time ensures the completion of transformation of ErH_{2+y} to ErH_{3-x} with simultaneous formation of magnesium hydride



As in the case of magnesium alloys with lanthanum and cerium, in the all-cast compact samples the first hydriding process takes place in a thin surface layer and powdering of the alloys to the 40–100 μm is required for its completion over the whole bulk.

In spite of the difference in the chemical nature of reactions (1) and (3) they both are associated with the diffusion processes of the metal-to-metal type. Therefore, in erbium alloys a decrease in temperature of the first hydriding may be due to an increased mobility of erbium atoms because of a smaller metal radius as compared with lanthanum and cerium.

As in the case of hydrogenolysis of intermetallic compounds the product of hydriding of a solid solution of erbium in magnesium is a mixture of binary hydrides. These compositions differ first of all by their microstructure and, hence, by the value of magnesium-rare-earth metal hydride interface area. The calculation based on microscopy data stereology has demonstrated that for compositions that contain 40 and 66 wt.% of lanthanum (the products of hydrogenolysis of intermetallic compounds are $\text{La}_2\text{Mg}_{17}$ and LaMg_3) $S_{\text{int.}}$ is respectively 10 and 22 m^2/g , while for the mixture formed in the course of decomposition of the solid magnesium-erbium (15%) solution it is less than 4 m^2/g . A decrease in the interface area naturally involves a decrease in the rate of interaction of these compositions with hydrogen (Fig. 4).

In order to elucidate the influence of rare-earth metals on the interaction with hydrogen of magnesium alloys we also investigated both magnesium-praseodymium and magnesium-neodymium alloys [7] (Table 1).

As is seen from the Table 1 we failed to achieve complete hydriding of specimens at 570–620 K. Even in the case of compositions corresponding to intermetallic such as LnMg_{12} the unreacted magnesium is present in hydrided pro-

ducts in contrast to similar cases of cerium-magnesium and magnesium-lanthanum alloys. As is seen from Fig. 5 the rate of hydrogen absorption by these specimens after activation is also lower than, for instance, for $\text{CeH}_{3-x} + 12\text{Mg}$, the lowest rate being observed for magnesium-praseodym alloys.

The reaction of the first cycle of hydriding of magnesium alloys has also been studied calorimetrically using CeMg_2 as an example. As is seen from the data presented in Fig. 5 the hydrogenolysis (1) is immediately preceded by the stage of hydrogen dissolution in a hydride matrix with the formation of a phase composition similar to CeMg_2H_2 . In the next stage, further hydrogen absorption is accompanied by hydrogenolysis with the formation of both magnesium and cerium hydrides. The enthalpy of hydriding and dehydriding of the products of CeMg_2 hydrogenolysis is -73.2 ± 1.9 kJ/mole at 489 K, and both the direct and reverse processes proceed with explicit hysteresis.

In order to elucidate the mechanism of the interaction with hydrogen of magnesium formed in the course of hydrogenolysis of intermetallic compound we have studied some more interactions with hydrogen of mechanical mixtures of magnesium with rare-earth metal hydride [8].

As was noted above, the first hydriding of magnesium-rare-earth-metal alloys involves the formation of an active binary hydride mixture with large interface area. A composition with similar ratio of constituents was also prepared using dispersed (about $40 \mu\text{m}$) individual phases by mechanical mixing in an inert gas. Activation of this mixture, i.e. achieving a reproduceable rate of interaction with hydrogen is possible only after 10 absorption-desorption cycles due to complicated morphological alterations in the system and powdering and loosening of particles. The specific surface area of the activated mixture does not exceed $2 \text{ m}^2/\text{g}$, while the surface area of the phase contact is substantially smaller, but it can be increased by compression (Fig. 7). The compacted specimens are distinguished by shorter periods of activation (2-3 absorption-desorption cycles).

In Fig. 8 are shown the hydriding curves for two-phase samples of the lanthanum magnesium hydride prepared by different methods. The highest rate of hydriding is inherent in a composition formed from alloys by reactions (1) and (2) with highest dispersity of phase constituents and most highly developed interface. The mechanical mixtures are distinguished by a marked increase in the rate of reaction after compacting. In this case the interface area is increased, the particle size being unchanged. A decisive importance of this

factor is also evidenced by an enhanced rate of hydriding with the increased amount of rare-earth metal hydride in the mixture which ensures the possibility of additional phase contact.

To elucidate the role of lanthanide hydride in the interaction with hydrogen of activated magnesium-rare-earth compositions and its influence on the mechanics of magnesium hydride formation, we carried out a formal kinetic analysis of the experimental data [9].

3. KINETIC ANALYSIS OF THE INTERACTION WITH HYDROGEN OF ALLOY TRANSFORMATION PRODUCTS IN MAGNESIUM-RARE-EARTH SYSTEMS

The "transformation degree vs. time" kinetic curves of hydriding (Fig. 4) show the highest rates for all compositions under study; the reaction rate increases with time and growing deviation of hydrogen pressure from the equilibrium Δp . Experimental data were processed using both Erofeyev-Avrami generalized topochemical (4) and model equations based on the mechanism of formation and phase boundary advance, or diffusion in solid.

$$[-\ln(1-\alpha)]^{1/n} = K_{E-A} \times \tau \quad (4)$$

$$-\ln(1-\alpha) = K_1 \times \tau; K_1 = K_1^0 \times e^{-E_1/RT} \times \Delta p \quad (5)$$

$$(1 - \frac{2}{3}\alpha) - (1-\alpha)^{2/3} = K_{11} \times \tau; K_{11} = K_{11}^0 \times e^{-E_{11}/RT} (\Delta p)^{0.6} \quad (6)$$

The calculated values of parameter n in equation (4) point to a possible change in the reaction kinetics and to the attainment of a diffusion control when transformation degree α is 0.3-0.7 (depending on composition and hydriding conditions); for interval of linearization of experimental data in the $F_1(\alpha) = K_1 \times \tau$ from is achieved when these stages are described respectively by the first-order equation (5) and by Hinstling-Brownstein equation (6). Kinetic parameters calculated by these equations are listed in Table 2.

Heterogeneous reactions for which the first-order equation can be applied are interpreted in the literature as a process limited by nucleation on a large number of small grains [10], while the mostly widespread concept is that hydriding of individual magnesium is limited by chemisorption or dissociation of molecular hydrogen on the metal surface [11-13]. This change in kinetics can be explained as follows.

Lanthanide hydride $\text{LaH}_{2.5-2.8}$ is a nonstoichiometric compound in which, according to statistics, hydrogen fills the holes in a crystal lattice. Under experimental conditions (560-630 K, 0.5-3.0 MPa) close to equilibrium for a particular composition the dissolved hydrogen exhibits an increased diffusive mobility. Affected by a chemical potential gradient on the external ($P_{\text{H}_2} = P_{\text{exp.}}$) and internal ($P_{\text{H}_2} = P_{\text{equ.}}$) surfaces the lanthanide hydride inclusions may serve as effective conductors of dissociated hydrogen to the magnesium surface, while the $\text{Mg}:\text{LaH}_{3-x}$ contact points are nucleation centers of magnesium hydride (Fig. 9). In this case a hydriding total rate is determined from the number of potential nucleation centers i.e. from the value of the interface area. Exactly this kind of experimentally determined relation has been noted previously for mechanical mixtures and alloy hydriding products in magnesium-rare-earth systems [5,8].

The determined dependence of rate constant on hydrogen pressure (5,6) makes it possible to calculate activation energy from temperature dependence of $\ln K_1$ with p being constant. The values obtained (Table II) represent apparent activation energy that include a sum of enthalpies of the stages supposed to be quasi-equilibrium [14]. According to this model of nucleation these stages are molecular hydrogen adsorption on the surface of the solid phase, dissociation of molecular hydrogen, and transition from the adsorbed to dissolved state. The total enthalpy of these reactions describing the process of hydrogen dissolution in metallic magnesium is 24 kJ/mole [15]. Taking into account this value, the true activation energy of nucleation may be estimated as 33-41 kJ/mole.

Transition to a diffusion control in the processes under consideration is, on the one hand, due to extremely low mobility of hydrogen in magnesium hydride and due to closing of internal pores and microcracks on account of volumetric phase expansion after hydriding, on the other. A certain contribution of molecular hydrogen transfer to diffusion process is indicated by the exponent in the pressure dependence of rate constant for the reaction final stage with the values as small as 0.25, 0.33, 0.5 in term of model representation based on complete dissociation of diatomic gas [14]. The use of Hinstling-Brownstein three-dimensional diffusion equation points to the absence in the system of explicit linear and two-dimensional transfer. For pre-eutectic alloys we failed to distinguish the stage limited by diffusion due to uneven distribution of magnesium grains with respect to their size and state of the

surface. Calculation of true diffusion activation energy from the value E_2 is complicated by lack in literature of necessary data on the enthalpy of hydrogen dissolution in magnesium hydride in particular.

According to the assumed model, the kinetic analysis allows one to determine possible ways of influencing the rate of hydriding of magnesium alloys containing rare-earth metals. In the nucleation stage it is introducing into the alloy the constituents that increase hydrogen solubility in magnesium or create additional nucleation centers. In the diffusion stage, a change in kinetic parameters is possible on account of constituents which are soluble in magnesium hydride and which increase the hydrogen diffusion coefficient in magnesium hydride or which change the alloy microstructure, i.e. which facilitate molecular hydrogen transport.

4. INTERACTION WITH HYDROGEN OF ALLOYS OF THE Mg-Ca-M (M- Al, Zn, Ce, Cu, Ni) SYSTEMS

The magnesium-calcium system might be a basis for hydrogen storage alloys. For this purpose we studied the interaction with hydrogen of alloys of the following ternary systems: magnesium-calcium-metal where metal is aluminium, zinc, cerium, copper or nickel and where the magnesium content exceeds 66 at.% [16-18]. The studies of the interaction with hydrogen of these alloys have revealed a general phenomenon, namely, all intermetallic compounds locating in this region of a phase triangle and entering into the composition of alloys (excluding Mg_2Ni) suffer hydrogenolysis according to known equations with magnesium hydride formation (Table III). Thus, hydriding of ternary alloys in the general case involves the formation of two morphologically different types of magnesium hydride grains which are the products of magnesium phase hydriding and of intermetallic compound hydrogenolysis. As a rule, it is followed by the formation of the ternary hydride $MgCaH_4$ instead of calcium hydride. In Figs. 10 and 11 are shown the curves of hydrogen absorption and desorption by samples after they have been repeatedly hydrided and dehydrided. As is seen from Fig. 10 a considerable hydrogen absorption rate may be reached only at 570-620 K. But even at this temperature the reaction rate is lower than for the samples of the magnesium-rare-earth system, although it exceeds greatly that for pure magnesium.

Decomposition of hydride phases proceeds with a clearly pronounced acce-

leration period and the curves have a sigmoid shape. It can also be noted that the alloys with zink have the lowest rate of both desorption of hydrogen in contrast to alloys with other additions. The activation energy of decomposition of magnesium hydride formed from magnesium-calcium-metal alloys is 72-105 kJ/mole.

Thus, the magnesium-calcium system can hardly be widely used as a basis of hydrogen storage alloys in spite of the fact that calcium is much more available than rare-earth metals because hydrogen absorption even by activated samples proceeds at fairly high temperatures. In view of this, we have concentrated basically on studying the interactions with hydrogen of ternary alloys containing magnesium and rare-earth metals.

5. INTERACTION WITH HYDROGEN OF ALLOYS OF THE Mg-Ln-M (Ln = Sc, Y, Ce, La, Mn, M = Al, Ni) SYSTEMS

Additional alloying of magnesium-rare-earth metals was necessary because of their inherent shortcomings that presented a substantial obstacle for practical use.

Firstly, in magnesium-rich intermetallic compounds with rare-earth metals, magnesium content does not exceed 60-65 wt.% which substantially (1.5-2 times) reduces the amount of accumulated hydrogen as compared with individual magnesium hydride. An increase in the amount of magnesium in excess of stoichiometric quantity sharply changes the kinetic mode of hydriding and reduces the process rate.

Secondly, the first hydriding of such alloys occurs only in the thin surface layer, and in order to make it complete through the whole bulk of the sample it must be powdered to 50-100 μm . Thirdly, the alloy hydriding rate sharply drops with temperature and even at 550-560 K the reaction cannot be carried out to completion even for several hours. Numerous attempts to improve sorption properties of magnesium alloys with rare-earth metals by their alloying with several metals have brought one to a conclusion that maximum effect can be reached by introducing aluminium and nickel [19-21].

In Mg-Ln-Al systems we have investigated the alloys with up to 8 wt.% of Al. Phase components of these alloys are magnesium, LnMg_{12} and LnMg_2 . As in the case of magnesium-rare-earth system, the first hydriding of these alloys starts at the grain boundaries; Mg-rare-earth intermetallic compounds are the

first to react with hydrogen and only after that the reaction proceeds over to the magnesium grains. The investigations have demonstrated that in system Mg-Ln-Al the alloys containing from 0,5 to 2,5 at.% of aluminium which is completely hydrided at 520-570 K are most promising. The sorption capacity of these alloys is described by the following equation:

$$\text{wt.\% of H(Mg}_x\text{Ln}_y\text{Al}_z) = \frac{2.016x + 3.024y - 1.512z}{26.328x + 143.144y + 25.477} \times 100\%, \text{ where } 2y > z \quad (7)$$

Figs. 12, 13 show the hydrogen absorption-desorption curves for activated samples of the magnesium-cerium-aluminium system. As is seen from Fig. 13, more than 2% increase in aluminium content in an alloy reduces the hydriding rate because a greater amount of cerium is bound due to the formation of CeAl_2 . High rates of hydrogen absorption are due to sinergetic influence of CeH_3 and CeAl_2 phases when their ratio is optimal. If CeH_3 is a donor of atomic hydrogen, the influence of CeAl_2 may be due to the fact that this compound offers an additional resistance to the magnesium grain growth and increases the inter-face area. An appreciable amount of hydrogen is absorbed by investigated samples even at room temperature.

As is seen from Fig. 13, the presence of CeAl_2 leads also to an increase in magnesium hydride decomposition rate. The decomposition curves are of definitely sigmoid character and are affine. The apparent desorption activation energy is 80-95 kJ/mole.

The greatest influence on the interaction with hydrogen of magnesium alloys with rare-earth metals is exerted by the introduction of nickel. The investigations carried out for magnesium-nickel-ittrium, scandium, cerium and misch-metal systems [3, 21] have demonstrated that such ternary alloys are hydrided practically to the end even at 420 K which has been noted in literature not only for pure magnesium but also for its binary alloys with nickel and rare-earth metals (Fig. 14). On the desorption isotherms there are two plateaus for all alloys under study. The plateaus that fully correspond to the phase composition also correspond to decomposition of magnesium hydride and Mg_2NiH_4 . Phase transformation heats in the plateau interval and dissociation equilibrium pressures of the corresponding hydride phases did not markedly differ from the data known from the literature which together with X-ray data point to the absence of mutual solubility in these systems.

We have paid special attention to determining the running characteristics of magnesium-rare earth-nickel-hydrogen systems. The investigations were carried out on alloys containing mischmetal as rare-earth metal. The advantages of mischmetal are its relatively low cost, as compared with pure lanthanides, and presence of constituent (iron, for example) the positive influence of which on magnesium hydriding has already been reported previously [22].

The most important characteristic of the composition for hydrogen storage is stability of its absorption characteristics after repeated hydriding and dehydriding. After 30 absorption-desorption cycles with the use of pure hydrogen the sorption capacity of the composition based on the magnesium-mischmetal-nickel keeps constant; the hydriding rate also remains unchanged (Fig. 15). But when commercial hydrogen containing 0.01% of oxygen is used, the sorption capacity is reduced monotonically, on average, by 0.5% per cycle. In this case magnesium oxide is found in the mixture. Calculations based on experimental data for the technological hydrogen storage systems have demonstrated that when the system is run a change in the sorption capacity due to oxidation of magnesium by additives in hydrogen is 1-2% per 100 cycles.

The established relationship allows one to make a comparative analysis of hydriding reactions of these ternary compositions in commercial and purified hydrogen. This analysis is based on the transformation of experimentally found "transformation degree-time" dependence with due regard for attainable maximum absorption (Fig. 16). The results of the analysis indicate that repeated absorption and desorption cycles in commercial hydrogen somewhat retards the hydriding reaction at the initial stage which is practically eliminated after the second treatment in purified hydrogen.

Thus, the influence of the impurities in commercial hydrogen on hydriding of magnesium-mischmetal-nickel alloys is reduced to two parallel processes, i.e. oxidation of magnesium incorporated in the composition that leads to a monotonic decrease in sorption capacity, and reversible change in the reaction kinetics at the initial stage due, apparently, to the surface adsorption processes.

6. INTERACTION WITH HYDROGEN OF INTERMETALLICS LnMg_2 ($\text{Ln} = \text{La, Ce, Er, Yb}$)

In alloys containing rare-earth metals the interaction of magnesium-rich intermetallic compounds are inevitably accompanied by hydrogenolysis (1). An-

other type of the interaction producing radiographically amorphous products is, according to the literature, associated with LaMg_2 [23]. We have investigated the aforesaid compounds of the two structural types: MgCu_2 (LaMg_2 , CeMg_2) [24] and MgZn_2 (ErMg_2 , YbMg_2). Although these compounds are chemically close to each other they substantially differ in character of the interaction with hydrogen.

At room temperature LaMg_2 and CeMg_2 absorb up to 6 hydrogen atoms per formula unit (H/f.u.). This is accompanied with tetragonal distortion of the cubic lattice of the initial intermetallics with 14% increase in the elementary cell volume. Under such conditions at the intermediate stage of hydriding LaMg_2 there was also observed a ternary hydride phase of the cubical system of LaMg_2H_2 composition.

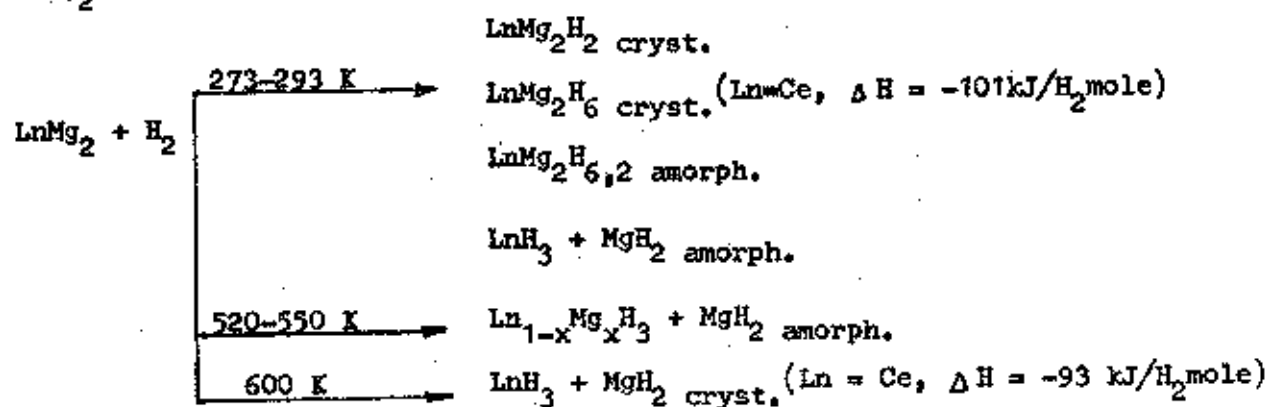
Hydriding of LaMg_2 at 523 K leads to decomposition of intermetallic compounds, but in this case the reaction product is lanthanum hydride with a decreased cell parameter ($a=0.556$ nm, $a_{\text{LaH}_3}=0.560$ nm); no reflections of magnesium-containing phases are observed on the diffractogram. This state may be considered as complete hydrogenolysis when, due to a reduced mobility of the metal atoms in the lattice (temperature is by 70–80 K below that typical for reaction (1)), magnesium is partly dissolved in lanthanum hydride, thereby lowering the lattice period and partly in radiographically amorphous state, apparently in the form of MgH_2 . Completion of hydrogenolysis, i.e. a complete separation of individual phases and their final crystallization occurs at 600 K.

The interaction with hydrogen of ErMg_2 proceeds in a similar way. In this case the formation of two ternary hydrides with 2 and 6 hydrogen atoms per one formula unit, respectively, is also typical, but the initial type of crystal structure is retained with only elementary cell parameter being increased. The difference in hydriding of LaMg_2 and ErMg_2 consists first of all in a decrease of temperature in the course of similar transformations. In the case of erbium-containing compounds the intermetallic matrices are decomposed in hydrogen gas even at room temperature, and this process can be prevented only by cooling the sample down to 273 K. But, as in the case of LaMg_2 and CeMg_2 , crystallization of the magnesium hydride phase crystallization is brought to completion only if hydriding temperature is raised to 600 K. This may be due to several factors. On the one hand, it is a higher enthalpy of formation of erbium hydride and, consequently of hydrogenolysis reaction as compared with those of

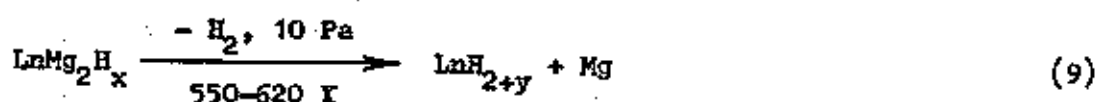
lanthanum hydride, and smaller erbium atomic radius that ensures higher diffusive mobility of erbium in magnesium alloy on the other (Table IV). The differences in diffusive mobility of erbium and lanthanum reside also in that for erbium hydride the formation of a magnesium-containing solution is not typical since the periods of the crystal lattice of the compound ($a = 0.3623$, $c = 0.6525$ nm) are similar to those for ErH_3 known from the literature.

The process is changed radically in the case of YbMg_2 . YbMg_2 does not interact with hydrogen till the temperature reaches 600 K, although a complete hydrogenolysis with the formation of ytterbium trihydride and magnesium hydride is observed. No-interaction in the $\text{YbMg}_2\text{-H}_2$ system at room temperature may be due to a large ytterbium atomic radius and lower enthalpy of trihydride formation. In contrast to lanthanum and erbium it may also be due to a reverse lanthanide-lanthanide interatomic distance relation in both intermetallic compound and individual metal. As is known from the literature data for various intermetallic compound hydrides, a considerable compaction of ytterbium atoms in YbMg_2 prevents hydrogen from penetration into the holes of the crystal lattice.

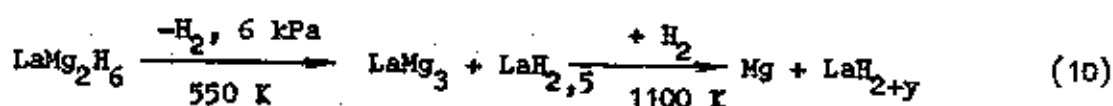
The experimental data we have obtained may provide an information on possible trends of the reactions in LnMg_2 -hydrogen systems. According to the crystal chemistry of the initial intermetallic compounds, hydriding of these compounds may be followed by the formation of both ternary phases and either partly or completely radiographically amorphous products whose composition and quantitative ratio depends on the temperature of the process and mobility of atoms in the metallic lattice. It should be emphasized that the enthalpy difference between hydrogenolysis and formation of ternary hydride determined for CeMg_2 calorimetrically does not exceed a few kcal/mole of H_2 .



All ternary hydrides synthesized in the LaMg_2 -hydrogen systems do not desorb hydrogen at room temperature and when heated in vacuum they decompose irreversibly to lanthanum hydride and magnesium



Only in the case of LaMg_2H_6 phase, the formation of magnesium-rich LaMg_3 compound stable up to the melting point of 1100 K was observed in the course of thermal decomposition under mild conditions (6 kPa) during which a partial resorption of separated hydrogen takes place



The presence of LaMg_3 in the products of LaMg_2H_6 pyrolysis may be due to the fact that of all binary intermetallic compounds in this system LaMg_3 is thermodynamically most stable.

REFERENCES

1. Semenenko K.N., Verbetsky V.N., Kochukov A.V. Doklady AN SSSR, 1981, v.258, N 2, p.362-366.
2. Semenenko K.N., Verbetsky V.N., Kochukov A.V., Sytnikov A.N. Vestn. MGU. Khimiya, v.24, N 1, p.16-27.
3. Klyamkin S.N., Kuliev S.I. "Materialy konf. mol. uchenykh knim. fak.MGU, Moscow, January 25-28, 1983, part 3". Moscow, 1983, p.383-386 (VINITI 28.12.1983, N 7085-83).
4. Verbetsky V.N., Klyamkin S.N., Semenenko K.N. Izv. AN SSSR, Neorgan. materialy, 1984, v.20, N 7, p.1126-1131.
5. Verbetsky V.N., Klyamkin S.N., Izv. AN SSSR. Metally, 1987, N 3, p.191-195.
6. Darriet B., Pezat M., Ebika A., Hagenmuller P. Mater. Res. Bull., 1979, v.14, N 3, p.377-385.
7. Semenenko K.N., Verbetsky V.N., Alyev B.Ch., Gasan-zade A.A., Kurbanov T.Kh. Azerb. khimicheskii zh., 1985, N 5, v.108-110.
8. Verbetsky V.N., Klyamkin S.N. Izv. AN SSSR, Metally, 1987, N 2, p.209-211.

9. Klyamkin S.N. "Materialy konf. mol. uchenykh khim. fak; MGU, Moscow, Jan. 25-28, 1985, part 1", Moscow, 1985, p.170-173 (VINITI 5.12.85, N 8373-B).
10. Mampel K.L. Z.Phys. Che. BFD, v. A187, p.43-57, 235-249.
11. Stander C.M. Z.Phys. Chem. BFD, v1977, v. 104, nN 4-6, p.229-238.
12. Lee J.J., Park H.H. Scr. Met., 1984, v. 18, N 11, p.1227-1230.
13. Gerasimov K.V., Ivanov E.Yu. Mater. Letters, 1985, v. 3, N 12, p.497-499.
14. Barret P. Cinétique hétérogène, Gauthier-Villars, Paris, 1973.
15. Popovic Z.D., Piercy G.R. Met. Trans., 1975, v. 6A, N 10, p.1975-1977.
16. Semenenko K.N., Verbetsky V.N., Kuliev S.I., Gasan-zade A.A. Zh. neorgan. khimii, 1983, v. 28, N 11, p.2948-2951.
17. Semenenko K.N., Verbetsky V.N., Sytnikov A.N. Vestn. MGU. Khimiya, 1984, v. 25, N 5, p.509-512.
18. Verbetsky V.N., Sytnikov A.N., Semenenko K.N. Zh. heorgan. khimii, 1984, v. 29, N 3, p.622-624.
19. Verbetsky V.N., Klyamkin S.N., Alyev B.Ch., Movlayev E.A. Izv. AN SSSR. Metally, 1986, N 3, p.189-193.
20. Semenenko K.N., Verbetsky V.N., Kochukov A.V. Red. Zh: "Vestn. MGU. Khimiya", Moscow, 1986. (VINITI 5.03.86. N 1491-B).
21. Semenenko K.N., Verbetsky V.N., Kuliyev S.I., Gasan-zade A.A., Kurbanov T.Kh. Zh. heorgan. khimii, 1984, v. 29, N 9, p.2192-2194.
22. Welter J.M., Rudman P.S. Scr. Met., 1982, v. 16, N 3, p.285-286.
23. Kost M.E., Raevskaya M.V., Shilov A.L., Yaropolova E.I., Mikheyeva V.I. Zh. neorgan. khimii, 1979, v. 24, N 12, p.3239-3243.
24. Verbetsky V.N., Klyamkin S.N. Izv. AN SSSR. Neorgan. materialy, 1987, v. 23, N 8, p.1303-1306.

TABLE I. COMPOSITION OF Mg-Pr AND Mg-Nd ALLOYS AND OF THEIR HYDRIDING PRODUCTS

N	Alloy composition wt. percent			Alloy phase composition	Amount of absorbed hydrogen	Phase composition of hydriding products
	Mg	Pr	Nd			
1	79	21		Mg ₁₂ Pr, Mg pre-eutectic	5.5	MgH ₂ , PrH ₃ , Mg
2	73	27		Mg ₁₂ Pr, Mg eutectic	5.2	- " -
3	67	33		Mg ₁₂ Pr	5.3	Mg, MgH ₂ , PrH ₃
4	79		21	Mg ₁₂ Nd, Mg pre-eutectic	5.9	MgH ₂ , NdH ₃ , Mg
5	73		27	Mg ₁₂ Nd, Mg eutectic	5.7	- " "
6	67		33	Mg ₁₂ Nd	5.4	Mg, MgH ₂ , NdH ₃

TABLE II: KINETIC PARAMETERS OF HYDRIDING OF TRANSFORMATION PRODUCTS
IN MAGNESIUM-RARE-EARTH ALLOYS

Alloy composition wt.%	T, K	ΔP , MPa	α_{1-2}	K_1 , min ⁻¹	K_2 , min ⁻¹ 10 ⁻¹
85 Mg-15La	528	1.0	0.05	0.17	
	548	1.0	0.10	0.29	
	598	1.0	0.25	0.90	
	613	1.0	0.30	1.30	
	598	0.5	0.20	0.44	
	598	2.0	0.35	1.85	
$E_1 = 60 \pm 6$ kJ/mole					
60 Mg-40 La (La ₂ Mg ₁₇)	523	1.0	0.15	0.21	0.10
	568	1.0	0.20	0.60	0.20
	598	1.0	0.55	1.05	0.27
	613	1.0	0.70	1.66	0.33
	568	1.6	0.30	0.99	0.27
	568	3.2	0.55	1.90	0.41
$E_1 = 57 \pm 5$ kJ/mole			$E_2 = 35 \pm 4$ kJ/mole		
34 Mg-66 La (LaMg ₃)	523	1.0	0.25	0.22	0.14
	548	1.0	0.40	0.43	0.20
	583	1.0	0.55	0.90	0.27
	613	1.0	0.75	1.71	0.39
	613	0.5	0.60	0.89	0.29
	613	1.5	0.80	2.50	0.45
$E_1 = 63 \pm 6$ kJ/mole			$E_2 = 30 \pm 3$ kJ/mole		
85 Mg-15 Er [Er] Mg	583	1.0	0.35	0.16	0.10
	608	1.0	0.40	0.25	0.14
	613	1.0	0.45	0.27	0.15
	633	1.0	0.60	0.40	0.19
	633	0.5	0.40	0.23	0.13
	633	1.5	0.65	0.58	0.23
$E_1 = 60 \pm 6$ kJ/mole			$E_2 = 34 \pm 3$ kJ/mole		

TABLE III: PHASE COMPOSITION OF Mg-Ca-M ALLOYS AND THEIR HYDRIDING PRODUCTS

N	System	Phase composition of initial alloys	Phase composition of hydriding products	Amount of stored reversible hydrogen, wt. %
1	Mg-Ca-Al	Mg, Mg ₂ Ca, Mg ₃ Al ₂	MgH ₂ , Al, MgCaH ₄	4.5-5.1
2	Mg-Ca-Zn	Mg, Mg ₂ Ca, Mg ₆ Ca ₂ Zn ₃	MgH ₂ , MgZn ₂ , MgCaH ₄	2.3-5.2
3	Mg-Ca-Ce	Mg, Mg ₂ Ca, CeMg ₁₂	MgH ₂ , CeH ₃ , MgCaH ₄	3.3-5.1
4	Mg-Ca-Cu	Mg, Mg ₂ Ca, Mg ₂ Cu	MgH ₂ , MgCu ₂ , MgCaH ₄	3.3-5.1
5	Mg-Ca-Ni	Mg, Mg ₂ Ca, Mg ₂ Ni	MgH ₂ , Mg ₂ NiH ₄ , MgCaH ₄	3.5-5.5

TABLE IV: LaMg₂ COMPOUNDS AND HYDRIDE PHASES BASED ON THEM

Intermet. comp.	Hydride comp.	Cell parameters, nm		La-La interatomic distance, nm		LaH ₃ hydride formation enthalpy - ΔH ₂₉₈ ⁰ kJ/mole
		intermet. compound	hydride	metal	intermet. compound	
LaMg ₂	LaMg ₂ H ₂	a=0.879	a=0.894	0.374	0.381	227
	LaMg ₂ H ₆	-"-	a=0.638 c=0.953			
CeMg ₂	CeMg ₂ H ₆	a=0.873	a=0.637 c=0.952	0.364	0.378	229
ErMg	ErMg ₂ H ₂	a=0.600 c=0.971	a=0.611 c=0.980	0.350	0.365	261
	ErMg ₂ H ₆	-"-	a=0.627 c=1.014			
YbMg ₂	-	a=0.619 c=1.003	-	0.388	0.380	195

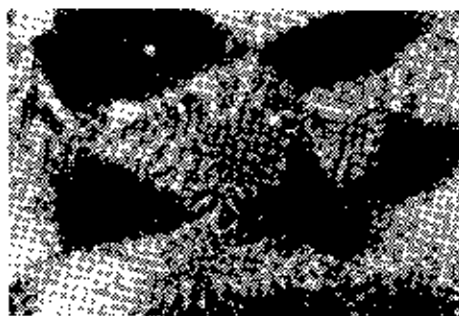


Fig. 1. Microstructure of hydriding products of intermetallic compound $\text{La}_2\text{Mg}_{17}$ in alloy Mg-15%La.

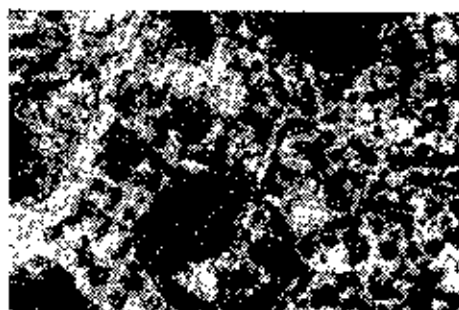
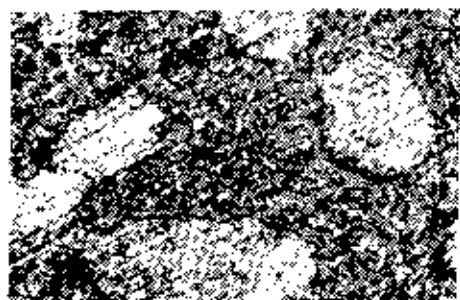


Fig. 2. Microstructure of hydriding products of pre-eutectic alloy Mg-15%La: a - initial step, b - final step.

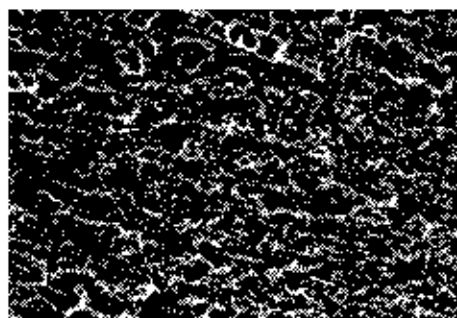


Fig. 3. Microstructure of hydriding products of erbium solid solution in magnesium (Mg-15%Er.);

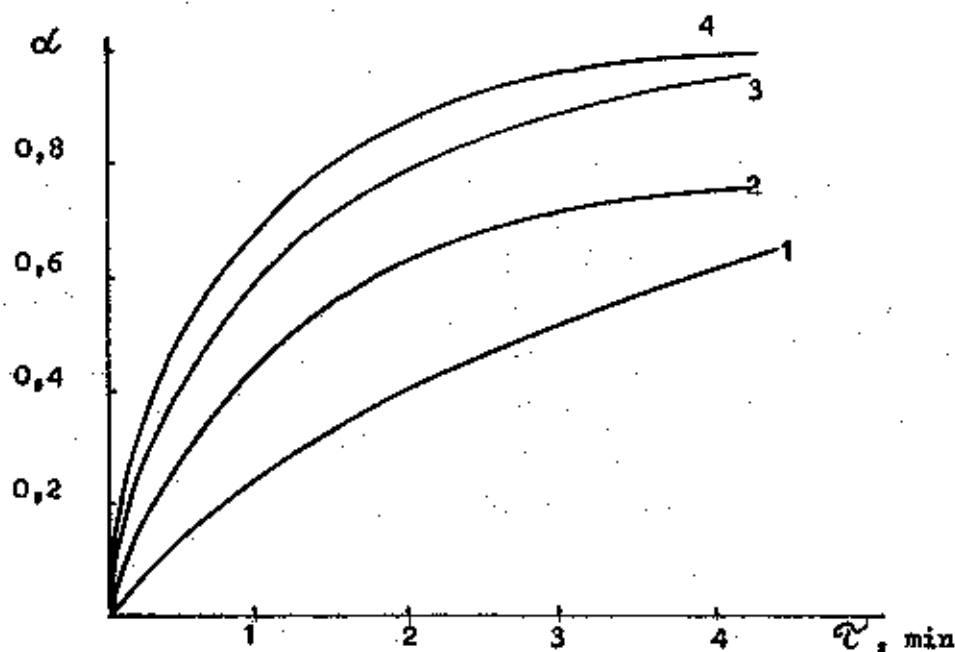


Fig. 4. Kinetic curves of hydrogen absorption by alloy transformation products in Mg-La and Mg-Er systems (613 K, 1,4 MPa): 1 - Mg-15%Er, 2 - Mg-15%La, 3 - Mg-40%La ($\text{La}_2\text{Mg}_{17}$), 4 - Mg-66%La (LaMg_3).

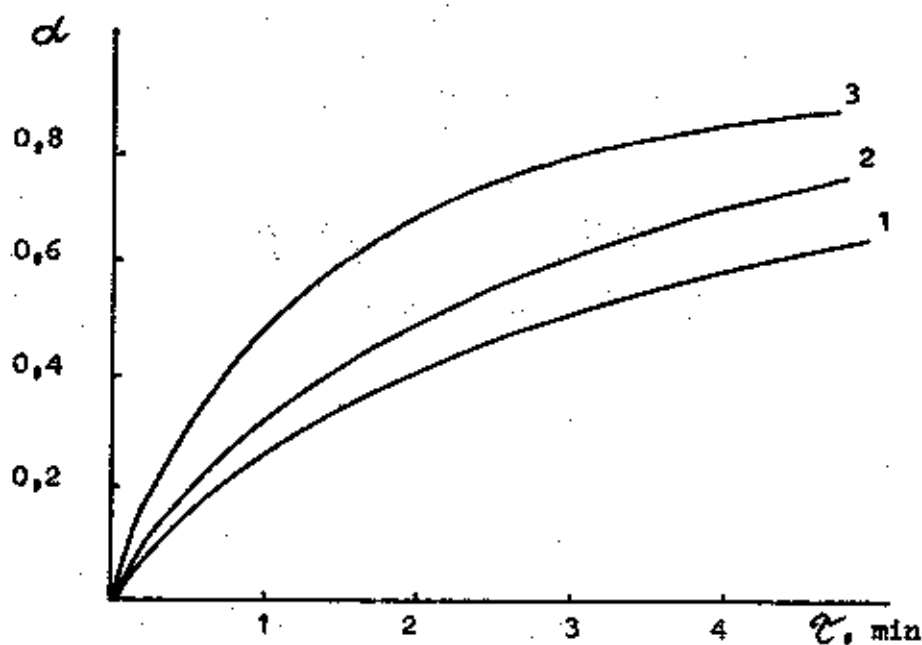


Fig. 5. Kinetic curves of hydrogen absorption by alloy transformation products in Mg-Pr, Mg-Nd and Mg-Ce systems (613 K, 1,4 MPa): 1 - Mg-33%Pr (PrMg_{12}), 2 - Mg-33%Nd (NdMg_{12}), 3 - Mg-33%Ce (CeMg_{12}).

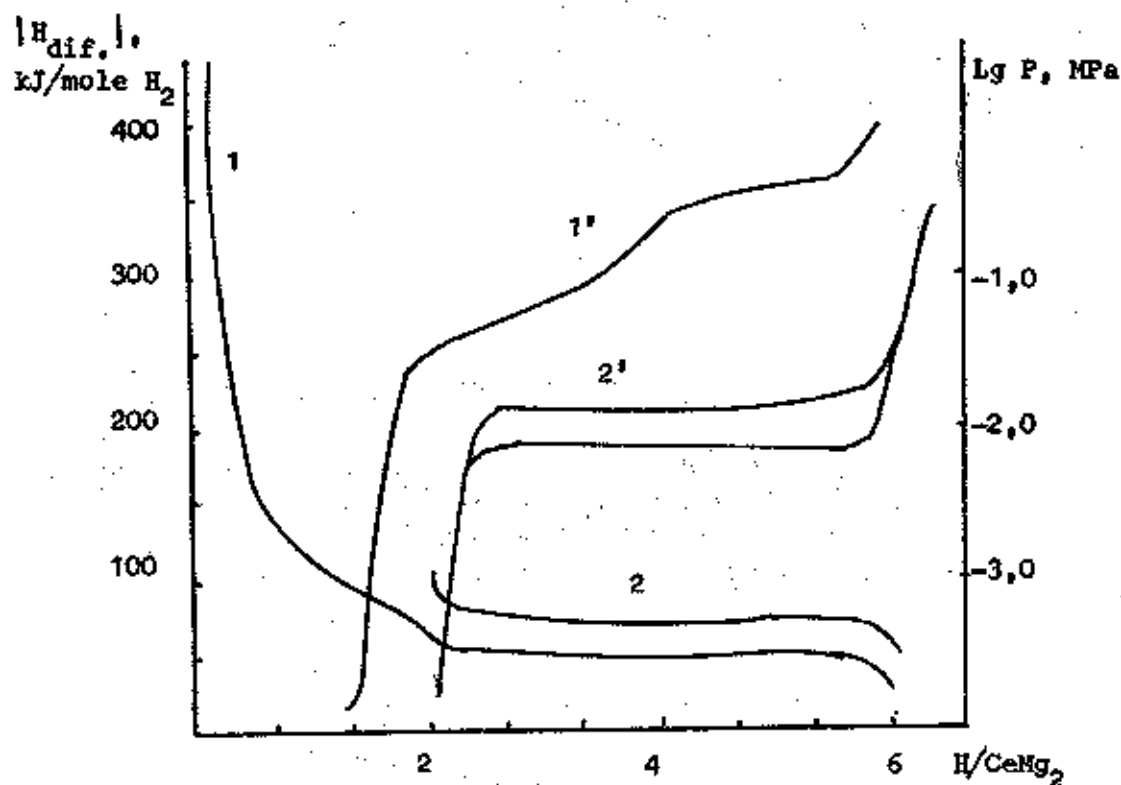


Fig. 6. Differential enthalpy and equilibrium hydrogen pressure for first hydriding of CeMg_2 at 536 K (curves 1 and 2) and for CeMg_2 transformation products at 489 K (curves 1' and 2').

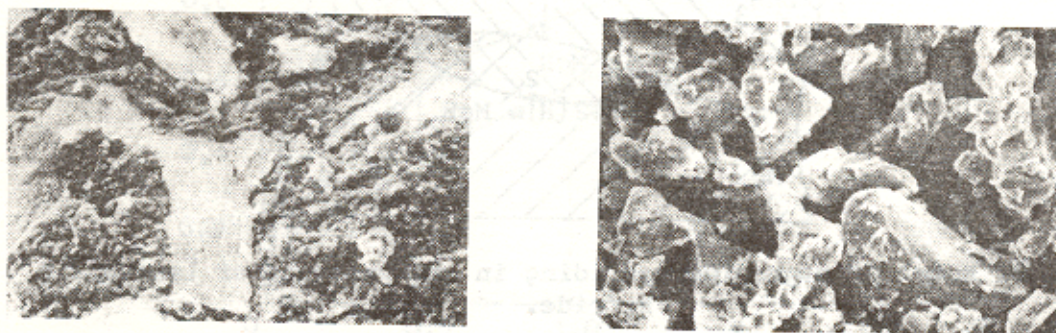


Fig. 7. Morphology of mechanical mixture (1) and hydriding products of alloy (2) in Mg-La-H system.

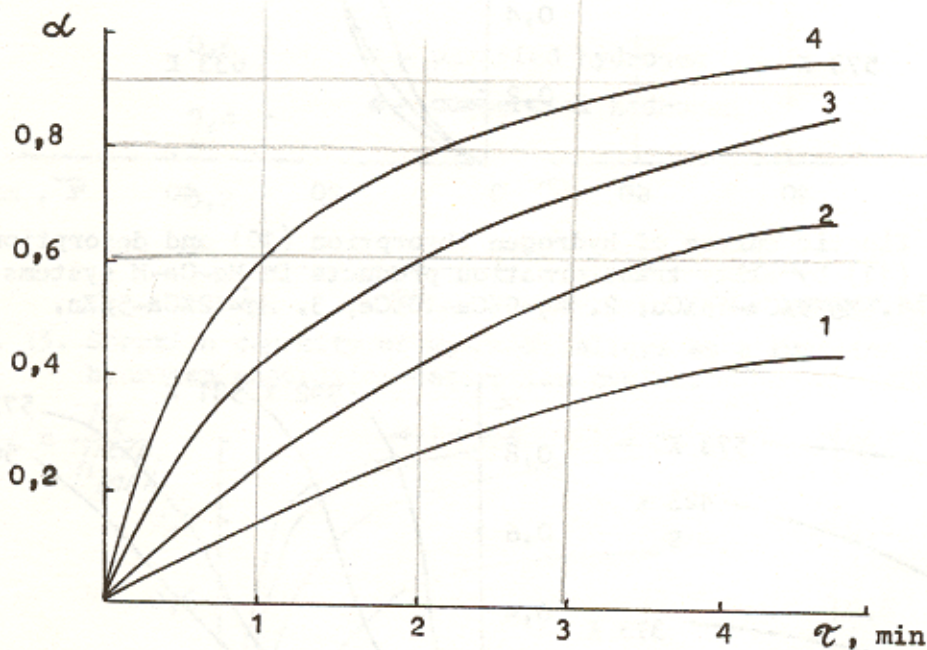


Fig. 8. Kinetic curves of hydrogen absorption by mechanical mixtures of Mg-La hydride (1-3) and by transformation products of $\text{La}_2\text{Mg}_{17}$ alloy (4) at 613 K, 1,4 MPa: 1 - [Mg-40%La], 2 - [Mg-60%La], 3 - [Mg-40%La]_{comp.}, 4 - Mg-40%La ($\text{La}_2\text{Mg}_{17}$).

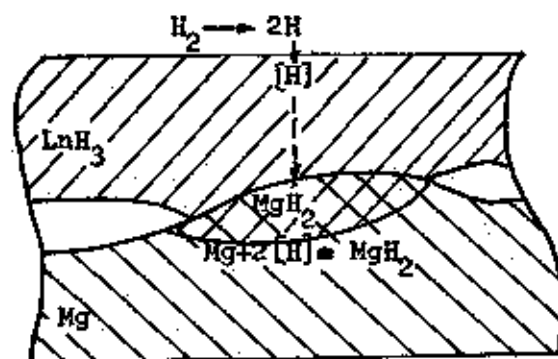


Fig. 9. Model of magnesium hydriding in the presence of lanthanoid hydride.

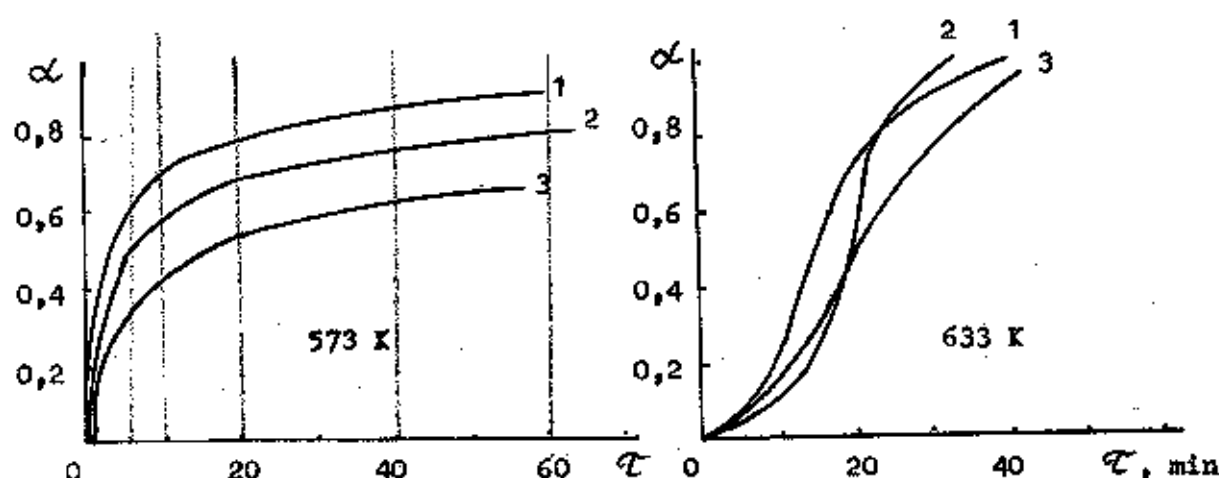


Fig. 10, 11. Kinetic curves of hydrogen absorption (10) and desorption (11) by alloy transformation products in Mg-Ca-M systems. 1. Mg-9%Ca-15%Cu; 2. Mg-9%Ca-10%Ce; 3. Mg-12%Ca-5%Zn.

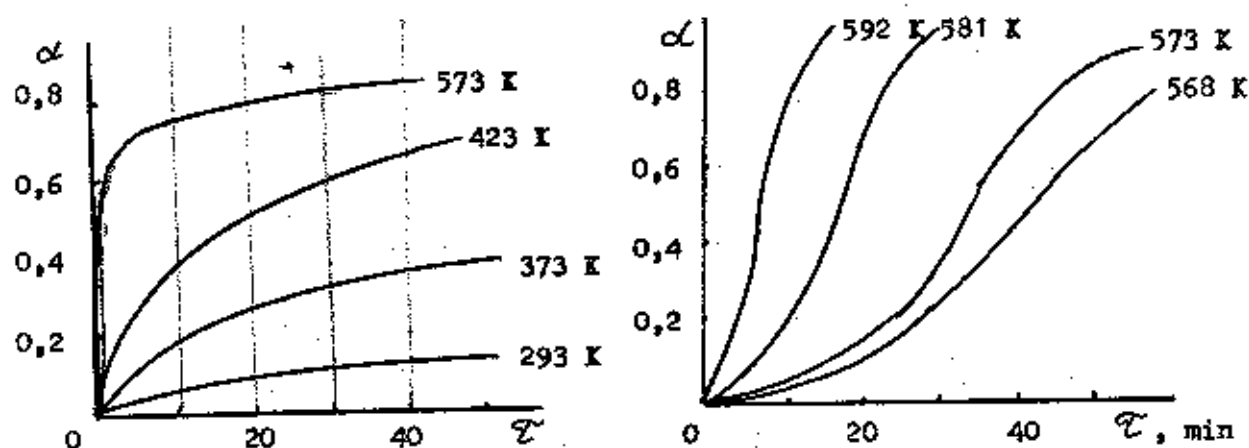


Fig. 12, 13. Kinetic curves of hydrogen absorption (12) and desorption (13) by products of transformation of alloy Mg-26%Ce-2%Al.

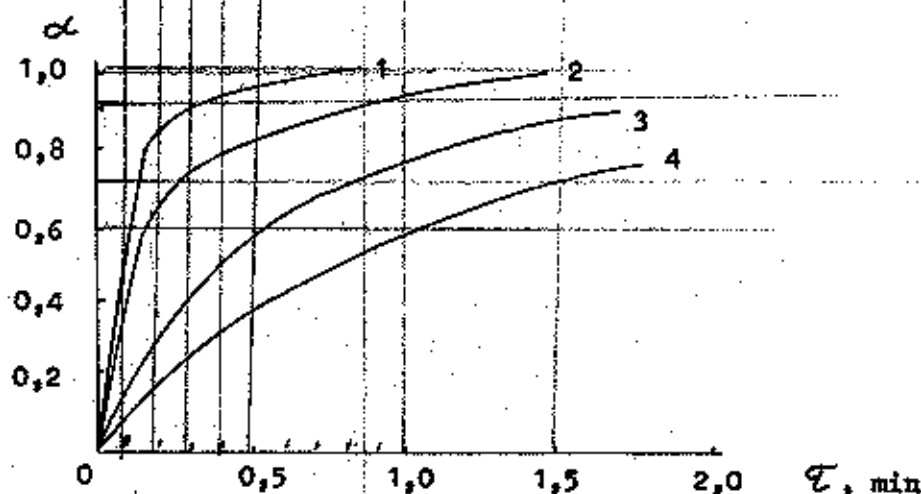


Fig. 14. Kinetic curves of hydrogen absorption by alloy transformation products in Mg-In-Ni systems (573 K, 1.0 MPa).

1. Mg-8%Mn-17%Ni; 2. Mg-8%Ce-17%Ni; 3. Mg-6%Y-19%Ni; 4. Mg-3%Sc-22%Ni.

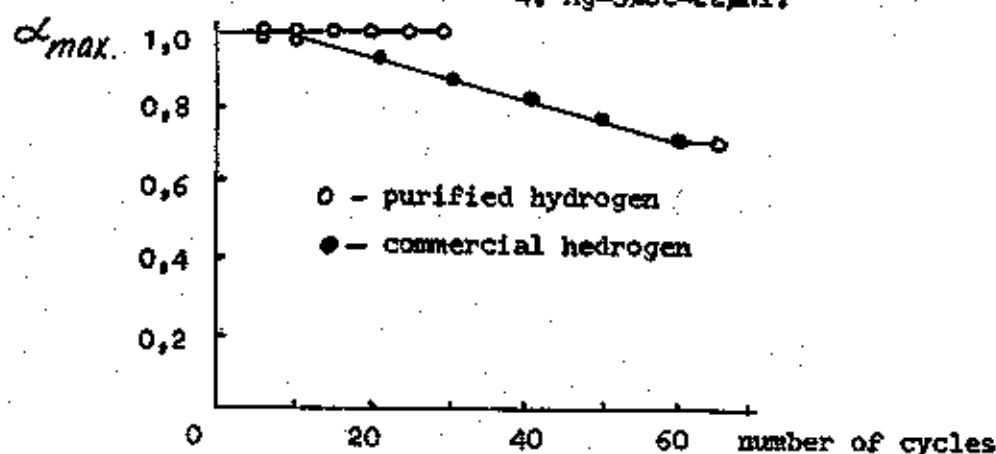


Fig. 15. Sorption capacity of Mg-Mn-Ni alloys as a function of number of hydrogen absorption-desorption cycles.

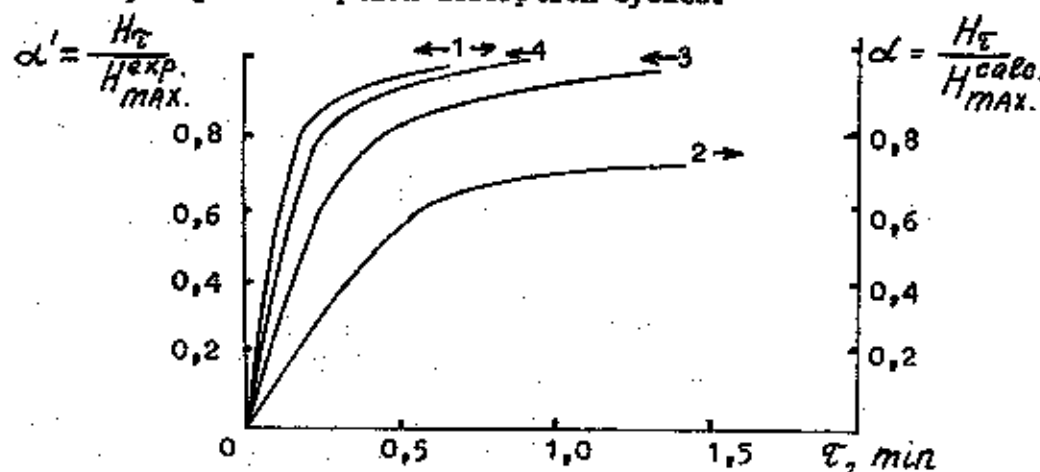


Fig. 16. Kinetic curves of hydrogen absorption by products of transformation of alloy Mg-8%Mn-17%Ni (573 K, 1.0 MPa); 1, 4 - purified hydrogen, 2, 3 - commercial hydrogen.