Hydrogenation of nanostructured alloys and composites based on magnesium

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The capability of sorbing hydrogen was studied for the magnesium alloys and related composites. The microstructures of the Mg—Ni binary eutectic alloys and Mg—La—Ni and Mg—Mm—Ni ternary eutectic alloys were studied. Both the initial alloys and alloys modified by the method of equal channel angular pressing were used as objects of the study. Features of interaction of the alloys with hydrogen were revealed. Sorption of hydrogen by the metal hydride composites based on alloys and "pseudoalloys," *viz.*, alloys obtained by sintering of mechanochemically treated highly dispersed powders formed by the hydride dispersion of metallic phases, was studied. Metal—carbon composites based on highly dispersed magnesium alloys or pseudoalloys and carbon nanostructures were formed, and the absorption of hydrogen by these composites was examined.

Key words: hydrogen, metal hydrides, magnesium alloys, eutectic, carbon structures nanocomposites.

Magnesium hydride has a high hydrogen sorption capacity (7.6 wt.%), but both sorption and desorption of hydrogen can occur only at elevated temperatures close to $300 \,^{\circ}$ C.¹ Processes of hydrogen evolution are associated with a high energy consumption because of the high enthalpy of magnesium hydride dissociation. The rates of heat and mass transfer of powdered materials prepared from magnesium hydride and capable of sorbing hydrogen are rather low. In addition, they are prone to sintering, which worsens the hydrogen sorption characteristics upon cyclic usage. The low sorption—desorption rate of hydrogen is among drawbacks of magnesium hydride as a material for reversible hydrogen storage. These are caused by several reasons.

First of all, the dissociation of a hydrogen molecule on the surface of magnesium particles has a high activation barrier² of ~50 kJ (mole of H₂)⁻¹. In order to improve the kinetics of hydrogen sorption—desorption, additives of transition 3d-metals, such as nickel^{3,4} and rare-earth metals (REM),^{5–8} are introduced into the magnesium-based materials. These additives catalyze processes of hydrogen dissociation on the surface of magnesium grains. Therefore, eutectic magnesium alloys with finely dispersed and homogeneously distributed phases, especially binary eutectic magnesium—nickel alloys, and ternary eutectic magnesium—REM—nickel alloys^{8,9} with the hydrogen capacity up to 5.5 wt.% are among the most promising materials for reversible storage of hydrogen. Such alloys can be obtained by usual melting, and investigation of their properties attracts attention of researchers.¹⁰ The mechanochemical methods for the preparation of magnesium-based alloys and composites with additives of transition 3d-metals, $^{11-14}$ transition metal oxides, 15,16 REM, 11 intermetallic compounds, $^{17-19}$ and various carbon materials $^{20-25}$ are also efficient.

At the same time, it was shown^{26,27} that hydrogen diffusion through the hydride phase MgH₂ was slow. So, at 300 °C, the diffusion coefficient is estimated at about 10^{-18} m² s⁻¹.²⁷ Therefore, a substantial increase in the hydrogen sorption rate can be attained when using nanostructured magnesium alloys and composites.^{28–32}

The methods of severe plastic deformation, namely, equal channel angular pressing (ECAP), are used to attain the nanostructured state of magnesium and its alloys.^{33,34} Such an approach makes it possible to prepare alloys in which the grain size is reduced to the submicronic or nanometric range and the density of interphase and intergrain boundaries is increased. This increases the rate of hydrogen interaction with magnesium alloys.^{33,35,36}

To improve the interaction of magnesium-based materials with hydrogen, we developed and used unique procedures of preparation of magnesium "pseudoalloys" and composites of these alloys with additives of carbon materials (thermoexpanded graphite, carbon nanofibers). The properties of the prepared materials were studied in processes of hydrogen sorption—desorption.

A complex approach combining X-ray diffraction analysis, optical microscopy (OM), scanning electron micro-

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scopy (SEM), electron probe X-ray microanalysis (EPXMA), and hydrogen etching method was used for the detailed study of the microstructure of the eutectic magnesium alloys.

Experimental

Metals of the following purity were used as the initial components for melting alloys (%): magnesium, 99.95; nickel, 99.99; and lanthanum, 99.79. In addition, misch metal of the following composition was used: 50% Ce, 27% La, 16% Nd, 5% Pr, and 2% of other REM. For the preparation of the binary eutectic alloy in the Mg—Ni system, the initial components were taken in the weight ratio 77% Mg and 23% Ni (hereinafter, alloy Mg—Ni). In the case of the ternary eutectic alloys in the Mg—La—Ni and Mg—Mm—Ni systems, the weight ratio of the initial components was 72% Mg + 8% La + 20% Ni and 72% Mg + 8% Mm + + 20% Ni (hereinafter, alloys Mg—La—Ni and Mg—Mm—Ni), respectively. The alloys were prepared in a crucible furnace under a flux.³

For metallographic investigation of the microstructure of the alloys, sections of their ingots were prepared by grinding and polishing. Some of the specimens were additionally subjected to chemical etching prior to OM studies. The quality of the alloys was estimated by the X-ray diffraction method (on powdered samples) and SEM, including EPXMA on metallographic sections of compact samples. The amounts of the corresponding phases in the eutectic Mg—La—Ni and Mg—Ni alloys were determined by the recalculation of the elemental analysis data obtained by EPXMA.

The microstructure of the alloys was studied by the OM methods using an Aristomet Olympus BX51M light microscope, high-resolution secondary electron SEM and EPXMA using Zeiss Supra 35 and Jeol JSM-5310LV microscopes equipped with Oxford Instruments and EDS Noran attachments, respectively, for measuring X-ray radiation with energy dispersion; EPXMA was carried out at an accelerating voltage of ~10 keV, and the relative content of elements in the alloy was calculated using the PROZA correction algorithm.³⁷

For the modification of the structure, the alloys were subjected to ECAP carried out in a die with an angle between the channel of 90°. Multiple pressing of the Mg—Ni alloys was carried out *via* the route, according to which the sample is rotated 180° around its longitudinal axis after each pressing. For the Mg—Mm—Ni alloys, the pressing followed the route, according to which the rotation angle was $+90^{\circ}$. Such parameters of the process as the temperature, the pressing velocity, and the number of pressings were varied.

Since the ECAP process was carried out along one chosen direction, the microstructure of the alloys changed anisotropically. This results in the appearance of the texture in the alloys modified by the ECAP method, which is confirmed, for example, by the analysis of the X-ray spectra obtained from the surfaces of compact samples of the ECAP-modified binary eutectic magnesium alloys. The relative intensities of the diffraction peaks of the same phase of a given sample were often different when the diffraction patterns were obtained from different cross sections of the sample: if one of them was parallel to the pressing direction and another was perpendicular to this direction. Due to this further comparative studies of the microstructure of the ECAP- modified alloys were carried out on metallographic cross sections made in the same orientation to the pressing direction.

The X-ray diffraction study was performed on a STOE diffractometer (Cu-K α radiation). The X-ray diffraction spectra were detected from both powdered samples and metallographic sections of the compact samples. For *in situ* high-temperature time-resolved X-ray diffraction analysis, an inert gas chamber was used equipped with the gas inlet and outlet, a temperatureprogrammed heater, a temperature regulator, and beryllium windows. Powdered samples of the hydrides of the fraction <90–120 µm in size were placed in the chamber. The specified temperature of the sample was achieved in the chamber within ~1 min. For each sample, ~20 spectra were recorded. The optimum recording conditions were determined: the range, increment, and integration time.

Powdered samples of the alloys were prepared by the method of hydride dispersion described earlier.³⁸ The pseudoalloy was obtained by sintering at 350 °C of a mixture of hydrides MgH₂, MmH₃, and Mg₂NiH₄ in the weight ratio corresponding to that of three hydride phases: the components of the hydrogenated ternary eutectic alloy Mg–Mm–Ni. The thermal analysis of the pre-dehydrogenated pseudoalloys shows the endotherm in the DSC curve. The minimum of the peak is observed at 500 °C, which corresponds to the melting point of the pseudoalloy and coincides with the melting point of the ternary eutectic Mg–Mm–Ni alloy obtained by the standard method.

The carbon nanofibers (CNF) were synthesized by the pyrolysis of ethene using hydride of intermetallic compound $LaNi_5$ as a procatalyst and purified from metals by washing in hydrochloric acid. This procedure was described in detail in the previously published work.³⁹ The thermoexpanded graphite (TEG) was kindly provided by the Chair of Chemical Technology and New Materials of the M. V. Lomonosov Moscow State University.

Powdered composites of the pseudoalloy with 10 wt.% TEG or nanofibers were formed by the treatment in a Pulverizette-6 planetary ball mill (Fritsch) at a rate of 500 rpm in an argon atmosphere. The balls to sample weight ratio was \sim 50 : 1. The milling duration was varied from 30 min to 16 h.

Polymetallic hydride composites were prepared under a hydrogen pressure of 10–30 atm by ball milling mixtures of powders of hydrides of either the initial or ECAP-modified eutectic magnesium alloys and intermetallic compound (IMC) La_{0.67}Mm_{0.33}Ni₅. The preparation was performed in a hydrogen medium under a pressure of 10–30 atm. The weight proportion of the composites was varied in a range of 80–95% of the hydrogenation product of the magnesium alloy + 20-5% La_{0.67}Mm_{0.33}Ni₅H_x. The ball milling conditions were as follows: the rotation rate ranged from 100 to 650 rpm, the ratio of the sample weight to the weight of the balls was from 1 : 1 to 50 : 1, and the milling duration ranged from 0.2 to 24 h.

The curves of hydrogen sorption—desorption by the studied materials were recorded by the volumetric method using a Sieverts setup.²⁰ Hydrogen elemental analysis was carried out by the combustion method using a Vario Cube elemental analyzer (Elementar GmbH). The specific surface was determined by the BET method from the low-temperature adsorption of nitrogen. The thermal analysis of the samples was performed on a high-vacuum setup by thermal desorption spectroscopy and by the simultaneous TG—DTA/DSC analysis and quadrupole mass spectrometry of the gas phase using an STA 409 Luxx instrument

(Netzsch). Heating was carried out with a constant rate of 5 or 10 deg min^{-1} in an argon flow.

Results and Discussion

The elemental and phase compositions of the initial binary and ternary eutectic alloys Mg—Ni and Mg—La—Ni presented in Table 1 correspond to the published data.^{40,41} The parameters of the ECAP process used for the modification of the samples of the Mg—Ni and Mg—Mm—Ni alloys are listed in Table 2. The designations of the samples (see Table 2) will be used hereinafter.

The X-ray phase analysis of both the initial and ECAPmodified samples of the Mg—Ni alloys (Fig. 1) indicates the presence of two phases, *viz.*, Mg and Mg₂Ni, which corresponds to the binary eutectics at the ratio of the components of the Mg—Ni alloys given in Table 1. Three phases are present in both the initial and ECAP-modified Mg—La—Ni alloy: Mg, Mg₂Ni, and La₂Mg₁₇ corresponding to the ternary eutectics at the ratio of the components of the alloy (see Table 1).

The metallographic studied of the initial and ECAPmodified eutectic alloys Mg—Ni, Mg—La—Ni, and Mg—Mm—Ni carried out by X-ray diffraction analysis and the OM, SEM, and EPXMA methods and supplemented by the hydrogen etching method⁴² made it possible to obtain the data on the elemental composition "at the point" and "along the line," to perform elemental mapping, and to determine the microstructure of the alloys.⁴³

Since it is farily difficult to obtain EPXMA data on the elemental composition of the eutectic alloys described in this work, let us consider the procedure of this analysis in more detail. In the case of EPXMA "at the point," the detector detects the characteristic X-ray radiation emitted from the volume which has the size of the excitation zone created by the incident electron beam, *i.e.*, several cubic microns.³⁷ This means that the data on the relative elemental composition "at the point" obtained for a finely grained sample are contradictory. More reliable information "from the point" can be obtained if the size of a probed

Table 1. Elemental and phase compositions (wt.%) ofthe Mg-Ni and Mg-La-Ni alloys

Component	Mg—Ni	Mg—La—Ni			
	Elements				
Mg	80.0±1.3	71.8±0.5			
Ni	20.0 ± 1.4	20.1±0.4			
La	—	8.1±0.3			
	Phases				
Mg	63.4±1.7	43.1±0.8			
Mg ₂ Ni	36.6±2.6	36.8 ± 0.7			
La_2Mg_{17}	_	- 20.1±0.8			

Table 2. Parameters of the process of equal channel angular pressing for the samples of the Mg—Ni binary eutectic alloy and Mg—Mm—Ni ternary eutectic alloy

Designation of alloy	Eutectic alloy	<i>T</i> /°C	u^a /mm min ⁻¹	N ^b
ECAP2×4	Mg—Ni	300	15	4
ECAP2×1	Mg-Ni	250	10	1
ECAP3×2	Mg-Mm-Ni	400	10	2
ECAP3×8	Mg-Mm-Ni	400	10	8

^{*a*} Pressing speed.

^b Number of pressings.

homogeneous inclusion is rather large compared to the size of the excitation zone.

However, the averaged EPXMA performed over an area of ~100×100 μ m does not provide reliable information either. The matter is that the PROZA algorithm makes it possible to calculate the ZAF coefficients necessary for the determination of the chemical composition under the assumption that the atoms of the calculated elements are homogeneously mixed in the sample. This is not true in our case, where the structure of the alloys is heterogeneous in a scale of 1 μ m. More reliable results can be obtained at a lower accelerating voltage of the electron microscope, when the ZAF coefficients for the characteristic lines of the components are approximately equal and close to 1.

The OM data indicate the highly dispersed structure of the eutectic Mg—Ni alloys modified by the ECAP method.³⁵ Insignificant inclusions of the third phase as solid dark polygons are observed in the microphotograph (Fig. 2). This phase is not identified by X-ray diffraction analysis and optical microscopy, and we used additional metallographic studies by SEM and EPXMA. The data obtained by these methods³⁵ indicate that the binary eutectic alloys Mg—Ni modified by the ECAP method have predomi-



Fig. 1. X-ray diffraction pattern of the powdered alloy $ECAP2 \times 4$; *I*, phase of Mg, and *2*, phase of Mg₂Ni.



Fig. 2. Optical micrograph of the alloy ECAP2×1. Etchant: a mixture of concentrated HNO₃ (1 mL), water (24 mL), and ethylene glycol (75 mL).

nantly lamellar highly dispersed structures (Figs 3 and 4). These lamellar domains belong to the binary eutectic Mg and Mg_2Ni phases. Inclusions of the third phase as light (in secondary electrons for the SEM images) solid polygonal domains are also present in insignificant amounts. The EPXMA method "at the point" showed that these inclusions were the MgNi₂ phase. It is known from literature data that the MgNi₂ phase is absent from the eutectic



Fig. 3. Micrograph of the alloy ECAP2×1.



Fig. 4. Micrograph of the alloy ECAP2×4.

alloys of this composition as well as from the initial, *i.e.*, unmodified by the ECAP method binary eutectic alloys Mg—Ni. Since no peaks corresponding to the MgNi₂ phase are observed in the diffraction patterns of the samples, it is evident that this phase is present in the alloys in very small amounts.

The microstructure of the alloys can be changed by the variation of the parameters of the ECAP process. For instance, in the case of the Mg—Ni alloy, an increase in the temperature and number of pressings during the ECAP procedure results in the more dispersed character of the eutectic component of the alloy (*cf.* Figs 3 and 4). It is most likely that the sizes of phase inclusions decrease and the extension of the interfaces increases, and the amount and character of inclusions of the third phase remains almost unchanged.

The microstructure and distribution of the component phases of the initial eutectic Mg–La–Ni alloy are not completely uniform in a range of 100 μ m.⁴² There are regions of two types in the initial alloy. The regions of the first type have the homogeneous microstructure in a scale of 10 μ m and include the Mg, Mg₂Ni, and La₂Mg₁₇ phases.⁴² In the SEM images (Fig. 5), the domains of the second type look like isolated uniform large spots and consist mainly of the La₂Mg₁₇ phase with inclusions of the Mg phase.⁴² The domains of the first type predominate on the images of the alloy, whereas the image in Fig. 5 was obtained for the domain of the second type.

Strictly speaking, the results of metallographic studies of the Mg–La–Ni and Mg–Ni alloys used in the present work do not allow one to consider them as truly eutectic. It can only be assumed that they correspond to eutectic alloys in the phase diagram. However, since the amounts of inclusions of the MgNi₂ phases in the Mg–Ni alloys and the domains of the second type in the Mg–La–Ni and Mg–Mm–Ni alloys are very small, they cannot



Fig. 5. SEM micrograph of the metallographic section of the alloy Mg–La–Ni. Circle shows the size of the projection onto the section plane of the excitation volume of the characteristic X-ray radiation.

change the conclusions drawn in this work about the influence of the structure of the eutectic Mg—Ni, Mg—La—Ni, and Mg—Mm—Ni alloys on their behavior during hydrogen sorption.

The ECAP treatment of the ternary eutectic magnesium alloy Mg—Mm—Ni results³⁶ in a substantial change in the microstructure of the alloy. For example, ECAP at 400 °C considerably decreased the sizes of inclusions of the phases and led to a greater homogeneity of the material. The most dispersed structure was observed after eight pressings.

Thus, the ECAP treatment enhances the dispersion of the alloy structure, enlarges the area of the phase and grain boundaries, and decreases the grain size of the phases. Both the phase and grain boundaries play the role of channels for hydrogen diffusion and, therefore, large total area of the interfaces facilitate hydrogen diffusion in the metal.

Let us consider features of the phase transformations occurred upon the interaction of the eutectic magnesium alloys with hydrogen. The features of the first stage of the interaction of the ternary eutectic Mg—La—Ni alloy with hydrogen was studied⁴⁴ by the methods of X-ray diffraction analysis of the compact sample surface and step-bystep hydrogenation developed in our group. In good agreement with other investigations,⁴ the hydrogenation results in the hydrogenolysis of the La₂Mg₁₇ phase, and the LaH₃ phase is formed much more rapidly than the MgH₂ phase. The hydrogenolysis of the intermetallic phase present in the initial alloy is irreversible in the considered case. This conclusion is not irrefutable. For instance, the LaMg₁₂ alloy was obtained by superfast cooling and the phase transformations occurred upon its interaction with hydrogen were examined.^{45,46} For this purpose, temperature-programmed desorption and high-temperature in situ timeresolved synchrotron X-ray diffraction were used. It was shown that hydrogen evolution from hydride of this alloy is accompanied by the recombination of intermetallic compound LaMg₁₂ from the hydride phases $LaH_3 + MgH_2$. The phases $LaMg_{12}$ and La_2Mg_{17} are nearly indiscernible by X-ray diffraction analysis used in the previous study,⁴⁴ where the conclusion about the presence of the La₂Mg₁₇ phase in the ternary eutectic Mg-La-Ni alloy was made. Additional studies are required to decide which of two intermetallic phases is present in the initial alloy.

We performed⁴⁷ a comparative analysis of hydrogen evolution from the hydrogenated alloys Mg—La—Ni and Mg—Mm—Ni by high-temperature *in situ* time-resolved X-ray diffraction. It was found that the replacement of lanthanum by misch metal substantially enhances the dynamics of hydrogen evolution, which follows from the change in the intensity of the X-ray diffraction peak of the magnesium hydride phase (Fig. 6). Since it is this phase



Fig. 6. Change in time of the intensity of the X-ray diffraction peak from the magnesium hydride phase (shown by arrow) in the hydrogenated alloys Mg–La–Ni (*a*, *b*) and Mg–Mm–Ni (*c*, *d*) on heating: T = 280 (*a*, *c*) and 300 °C (*b*, *d*).

that prevails in the mole ratio in the samples, the change in time of its content reflects the dynamics of hydrogen evolution from the samples. The content of the MgH_2 phase is most clearly shown by the intensity of the peak 110 in the diffraction pattern: this peak is the strongest and, in addition, it does not overlap with other peaks. Comparable times of decomposition of the crystalline phase of magnesium hydride in the hydrogenated alloy Mg—Mm—Ni are attained at temperatures ~20 °C lower than those for the hydrogenated Mg—La—Ni alloy.

Upon the hydrogenation of the modified alloy Mg–Ni, the formation of the magnesium hydride phase occurs more rapidly than in the case of the hydride phase Mg₂Ni. This is seen from the X-ray diffraction data obtained from the surface of a compact specimen of the alloy. After heating in a hydrogen atmosphere at 300 °C under 25 atm for 6 h, only a reflection of the MgH₂ phase is observed (Fig. 7). Note that, under these conditions, hydrogen also acts as an etching agent revealing intergrain boundaries in all inclusions of the MgNi₂ phase (Fig. 8, inset).

The ECAP-modified eutectic magnesium alloys Mg-Ni, Mg-La-Ni, and Mg-Mm-Ni can be shattered substantially more readily than the unmodified alloys. For the first hydrogenation (activation) of the ECAP-modified magnesium alloys, it is necessary to reduce their particle size to $\leq 200 \,\mu\text{m}$. It was found by an analysis of the curves of hydrogen adsorption and evolution by the powdered samples of the alloys that the ECAP-modified magnesium alloys Mg-Ni demonstrated a higher rate of interaction with hydrogen than the unmodified alloys (Fig. 9). This indicates that these modified alloys is a promising base for the development of materials with improved hydrogen sorption characteristics. Note that the higher rate of hydrogen sorption is characteristic of the initial region of the adsorption curve corresponding to the modified alloy, whereas the total amount of adsorbed hydrogen is the same



Fig. 7. Diffraction patterns obtained from the transversal metallographic section of the alloy ECAP2×1: *a*, initial metallographic section; *b*, section after storing in a hydrogen atmosphere (6 h, 300 °C, 25 atm); *1*, Mg; *2*, Mg₂Ni; and *3*, MgH₂.



Fig. 8. SEM micrograph of the metallographic section of the alloy ECAP2×4 after storing in a hydrogen atmosphere (6 h, $300 \,^{\circ}$ C, 25 atm). Inset: the image of the region containing the MgNi₂ phase (with a larger amplification). It is seen that the intergrain boundaries are extended due to hydrogen diffusion along these boundaries and to the interaction of hydrogen with the grain boundaries (so-called "hydrogen etching").

for the both samples. The rate of the interaction of the modified alloys with hydrogen increases after the highenergy treatment of these alloys in a planetary ball mill.

The addition of hydride of an intermetallic compound of the AB₅ type entails the polymetallic composite being hydrogenated with a higher rate than that of the initial eutectic magnesium alloy. We conducted a search for parameters of formation of polymetallohydride composites in terms of the hydrogen and dehydrogenation rate parameters of weight content of hydrogen and dehydrogenation rate. The search involved the treatment of the hydrogenated eutectic magnesium alloys with the hydride additive La_{0.67}Mm_{0.33}Ni₅H_x in a ball mill in a hydrogen medium. It turned out that the optimal parameters are as follows: composite composition 90 wt.% hydride of the magnesium alloy + 10 wt.% hydride of the intermetallic com-



Fig. 9. Curve of hydrogen consumption (*A*) at 350 °C and a hydrogen pressure of 20 atm by the alloy ECAP2×1 (*I*) and the initial alloy (*2*). The curves were recorded after five cycles of hydrogen sorption—desorption.

pound, milling duration 1 h at a rate of 500 rpm, and hydrogen pressure 30 atm. After several sorption—desorption cycles, the amount of hydrogen sorbed by the composites within the first 10 min achieves 5 wt.%. The data of temperature-programmable hydrogen desorption show that the temperature of hydrogen evolution from the hydrogenated composite is 60 °C lower than the temperature of hydrogen evolution from the hydrogenated eutectic magnesium alloy. An improved ability of the composites "hydrogen compared to the initial eutectic alloys is explained by the activation of hydrogen in the presence of the intermetallic compound.

Our method developed for the formation of "pseudoalloys" from a mixture of hydrides MgH_2 , MmH_3 , and Mg_2NiH_4 in the weight ratio corresponding to the ratio of three hydride phase (components of the ternary eutectic hydrogenated Mg—Mm—Ni alloy) turned out to be a very efficient procedure for the preparation of materials that are able to accumulate hydrogen.^{48,49}

Table 3 illustrates the influence of the duration of mechanochemical treatment and the type of carbon material on hydrogen sorption by the composites "pseudoalloy"—carbon. Hydrogenation was carried out at 300 °C under a hydrogen pressure of 20 atm. The amount of hydrogen sorbed in the first hydrogenation cycle was determined by thermogravimetry and chemical analysis. The value of temperature at which the DSC curves have a minimum (endotherm) was defined as the temperature of hydrogen evolution. The data obtained for the "pseudoalloy" without an additive of the carbon component are also giv-

Table 3. Effect of the duration of mechanochemical treatment (t) and the type of the carbon nanomaterial on the hydrogen sorption properties of the composites

Sample	<i>t</i> /min	$S^a/\mathrm{m}^2\mathrm{g}^{-1}$	A^b (wt.%)	<i>T</i> ^c /°C
Pseudoalloy	30	0.5	3.2	320
	60	0.9	3.5	300
	90	1.2	5.0	290
	300	0.9	4.3	300
	480	1.2	3.8	300
Pseudoalloy	30	7.5	4.2	300
+ 10 wt.%	60	9.0	4.2	290
TEG	90	19.4	5.1	300
	300	18.5	4.8	300
	480	15.0	3.8	300
Pseudoalloy	30	7.0	3.6	315
+ 10 wt.%	60	10.5	4.1	300
nanofibers	90	18.0	5.3	295
	300	17.4	4.3	300
	480	16.4	3.2	305

^a Specific surface.

^b Amount of hydrogen absorbed in the first cycle.

^c Temperature of hydrogen evolution.

en for comparison. It follows from the data in Table 3 that the presence of the carbon material increases the specific surface area of the composite by an order of magnitude. Although at the temperature of the experiment the carbon material itself sorbed much less hydrogen than the alloy, its additive in an amount of 10 wt.% makes it possible to increase the hydrogen sorption capacity of the composite in the first cycle. The duration of the mechanochemical treatment exerts a substantial effect on the amount of hydrogen sorbed in the first hydrogenation cycle and, to some extent, on the temperature of hydrogen evolution. The hydrogenation of the composites prepared by the mechanochemical treatment for 90 min with the addition of nanofibers occurs most rapidly. Although the specific surface area of these composites is somewhat lower, as a rule, than that of the composites "pseudoalloy"-TEG, the amount of hydrogen sorbed in the first cycle is higher (see Table 3). Evidently, at the initial stage, the elongation of the milling duration makes it possible to obtain a powdered material with an increased dispersity due to a decrease in the sizes of the composite particles. This is indicated by the data of particular experiments in which the powdered composites were obtained at different milling durations of a mixture of the hydrogenated binary eutectic Mg-Ni alloy with nanofibers (Fig. 10). A longer mechanochemical treatment induces the partial dehydrogenation of the powdered samples and cold-hardening of soft metallic particles of magnesium, which deteriorates the hydrogen sorption properties of the prepared materials and somewhat decreases the specific surface area of the composites.

A more comprehensive comparison of the composite materials subjected to the mechanical treatment for 90 min gives a series of conclusions about the influence of carbon material additives on the characteristics of the composites. For example, peaks of both magnesium hydrides and unhydrogenated magnesium appear in the diffraction pattern of the "pseudoalloy." An incomplete hydrogenation is also confirmed by the hydrogen sorption curves. In the



Fig. 10. Image of the composite hydride of the alloy Mg-Ni + 10 wt.% CNF prepared by planetary ball-milling for 1 h at 500 rpm.

presence of additives of TEG and carbon nanofibers, a 90% hydrogenation is observed already in the first cycle. The diffraction pattern of the hydrogenated composite with the TEG additive (after the first hydrogenation) contains peaks corresponding to three hydride phases: LaH₃, Mg_2NiH_4 , and MgH_2 . A similar pattern is also observed for the product of the first hydrogenation of the composite with the additive of carbon nanofibers. The introduction of carbon additives does not result in the formation of new phases in the composites. For instance, the X-ray diffraction data for the composite of the ECAP-modified binary eutectic Mg—Ni alloy with carbon nanofibers (milling under an argon atmosphere at a rate of 500 rpm for 1 h) show no carbide phases.

It follows from the character of the hydrogen sorption curves that the rate of H₂ sorption in the first hydrogenation cycle and the amount of sorbed hydrogen are somewhat higher for the composite "pseudoalloy"-nanofibers than those for the "pseudoalloy" itself.⁴⁹ However, the influence of carbon additives on a decrease in the dehydrogenation temperature of the composites "pseudoalloy"-TEG and "pseudoalloy"-nanofibers is insignificant (Fig. 11, see Table 3). The values of temperatures corresponding to the positions of minima in the DSC curves recorded at a heating rate of 10 °C min⁻¹ in argon differ noticeably for the hydrogenated Mg-Mm-Ni alloy, the pseudoalloy of the same composition, and the composite "pseudoalloy" nanofibers: 315, 290, and 285 °C, respectively (see Fig. 11). Thus, the temperature of hydrogen evolution on heating of the hydrogenated pseudoalloy is more than 20 °C lower than that in the case of the hydrogenated cast alloy. Hydrogen evolution from the hydrogenated composite "pseudoalloy"-nanofiber prepared by the mechanochemical treatment for 90 min occurs at the lowest temperature, but its value differs not more than by 5-10 °C from the temperature of H₂ evolution from the hydrogenated "pseudoalloy"



Fig. 11. DSC data (ΔQ) for the hydrogenated samples of the alloy Mg–Mm–Ni (*1*), pseudoalloy (*2*), and composites based on the pseudoalloy with graphite (*3*) and with the carbon nanofibers (*4*).

and hydrogenated composite "pseudoalloy"—TEG prepared under the same conditions.

The new approach to the formation of composite materials on the basis of the ternary eutectic Mg-Mm(La)-Ni "pseudoalloy" with carbon materials (TEG ad nanofibers)⁴⁹ makes it possible to form materials that are less prone to sintering during processes of hydrogen sorption and desorption at 300-350 °C and under the conditions of higher heat effects, which are characteristic of the reactions of the magnesium-based alloys with hydrogen.

It is most likely that the carbon materials acts as a "stabilizer" of the highly dispersed state of the hydrogensorbing alloy. The presence of carbon in the composite reduces sintering of the powdered samples during cycling. Probably, this occurs because the carbon material "isolates" metallic particles of the powder from each other and has a higher heat conductance than metal hydride. Possibly, the presence of the carbon material prevents the grain growth of the magnesium phase. The grain growth occurs during recrystallization in plastically deformed materials^{50,51} prepared by milling or ECAP at the same temperatures at which hydrogen interacts with the magnesiumbased alloys.

High-energy milling in a hydrogen atmosphere also favors the achievement of the best characteristics of the powdered materials during hydrogen sorption. For instance, the curves of hydrogen sorption by the binary eutectic ECAP-modified Mg—Ni alloy before and after milling in a hydrogen atmosphere were obtained in three consecutive cycles. An analysis of these curves shows³⁵ that after the mechanochemical treatment the material demonstrates approximately the same rate of hydrogen sorption in all the three cycles, whereas the initial alloy sorbs hydrogen with approximately the same rate but attains a constant value of the capacity for hydrogen only after several sorption—desorption cycles.

Thus, the following conclusions can be drawn after the studies carried out.

(1) The microstructure of both the initial and ECAPmodified Mg—Ni alloys was established, whose composition corresponds to the binary eutectics, as well as the Mg—La—Ni and Mg—Mm—Ni alloys, whose composition corresponds to the ternary eutectics.

(2) The regularities of the interaction of the initial and modified alloys with hydrogen were revealed. A suggestion was made that explains the influence of the modified structure of the eutectic magnesium alloys on their behavior during hydrogen sorption. It was established that the ECAP-modified binary eutectic magnesium alloys demonstrated a higher rate of hydrogen sorption compared to the unmodified eutectic alloys.

(3) The unique approach was developed to the formation of hydrogen-sorbing composite materials on the basis of the ECAP-modified magnesium alloys with additives of IMC La_{0.67}Mm_{0.33}Ni₅ and "pseudoalloys" with additives of carbon materials by the mechanochemical treatment under the ball milling conditions. These composites demonstrate a higher rate of interaction with hydrogen compared to the cast alloys.

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