Mechanical alloys Mg-Me (Me= Ti, Fe, Ni, Al) & Mg-Me₂(Me1=Al, Me₂= Ti, Fe, Ni) with low resistance and improved kinetics of hydrogenation/dehydrogenation for hydrogen storage applications

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Abstract

Changes in MgH2 decomposition kinetics were investigated in dependence on complex doping of MgH2 by Al, Ti, Ni,and Fe. Reactive mechanochemical alloying method (RMA) was applied in the temperature descending regime. It was found that addition of Al+Ni+Ti, Al+Ti, Fe+Ti (see below) and Al+Fe elements combinations led to a lower thermal stability and, consequently, to a lowering of the temperature of hydrogen desorption onset. Whereas desorption began at temperature of 320 °C from the pure MgH2, the aditions of Al, Ni, Ti and Fe lowered the start of the desorption down to 250°C (at hydrogen pressure 0.1 MPa in the reactor). Very fast desorption kineticsprecize at 300 ^{0}C and P_{H2}= 0.1 MPa were observed for Mg+Me mixture in comparison with the pure Mg. Sorption capacity of investigated mechanically-alloyed composites varied from 5 to 6.5 wt. % H2. The tested materials showed a high potential as hydrogen storage alloys especially for stationary application.

Introduction

The problem of syntheses of magnesium dihydride, MgH_2, with low temperature and high kinetics of its dissociation, high hydrogen capacity and cyclic stability (i.e., with characteristics that are very important for practical use of MgH_2) remains still unsolved, and investigations of solving this problem are of current interest. Therefore, among fundamental studies dedicated to Mg-based hydrogen-sorption materials carried our over the last decade, the most part of them was devoted to improving kinetics of processes of hydriding-dehydriding of the materials. Thermodynamic stability and decomposition temperature (at 0,1 MPa H_2) of MgH_2 still remain rather high for mobile use as hydrogen battery for vehicles. These shortcomings authors try to solve by commercial MgH_2 mechanical dispersion in the presence of various kinds of catalytic additives: transition 3d-, 4d-metals [1-11] and their oxides [12-24], fluorides [25], intermetallic compounds and additives of Al, Cu, Zn, In, Sn non-transition metals, graphite and others [26-38]. Many researchers follow the different way of Mg milling powder with pointed additives in hydrogen atmosphere (reactive milling) or in an inert atmosphere, followed by its direct hydrogenation from gas phase [39-77]. A small addition to magnesium of alloying element (about 10 at. %) provides a high MgH_2 hydride phase percentage and more than 5 wt. % hydrogen-capacity in the synthesized alloy-composite. Compared to MgH_2, magnesium alloys hydrides (Mg_2NiH_4 and other Mg-based ternary hydrides) are known to have not only low thermodynamic stability, but also significantly lowered hydrogen-capacity, that makes them less appropriate for practical application.

MgH_2, which is processed in the presence of the catalytic additives can significantly improve the kinetics of hydrogen desorption. Herewith, its thermodynamic stability and decomposition temperature (at 0,1 MPa H_2) still remain rather high for mobile use of these mechanically alloyed compositions as hydrogen battery for vehicles. One way to solve the problem of MgH_2 thermodynamic stability reducing (destabilization), which is considered by researchers in recent years [77-81], is the use of MA which are solid solutions in magnesium one or more metals capable to reduce the enthalpy of $Mg(Me)H_2$ decomposition. According to theoretical prognosis [9], hydride of Al, Ti, Fe, Ni, Cu, Nb solid solution in magnesium should have a lower enthalpy of formation and decompose at a lower temperature compared with pure MgH_2. A number of experimental studies indicate that this hydride solid solution thermodynamic stability depends on the method and conditions of its obtaining [77-82]. Thus, at hydrogen pressure in the reactor of 0,1 MPa the decomposition of $Mg(In)H_2$ hydride phase of mechanical alloy obtained in [81] by high-

energy grinding in ball mills of MgH_2 powder with the addition of 10 at.% In at a hydrogen pressure of 15 MPa begins at 262,3 ^0C. This temperature is 26 degrees lower than the temperature of MgH_2 decomposition without additives (288 ^0C), which testifies lower thermodynamic stability of $Mg(In)H_2$ formed hydride phase compared with pure magnesium hydride. It is established, that in the case of Mg + 8 at. % Al alloy [79] the addition of Al leads to absorption enthalpy decreasing from 79 to 72 kJ/mol. H_2, while desorption enthalpy is not changed, but entropy increases. XRD analysis of the initial Mg + 10at.% Al alloy [80] revealed Al solid solution in magnesium Mg (Al) formation, which turned into MgH_2, Al and a small amount of Mg_2Al_3 phases, as a result of its complete hydrogenation. According to P-C-T curves [80], hydrogen desorption from magnesium hydride of Mg + 10 at. % Al alloy starts at a relatively high equilibrium pressure of 2 MPa compared with the pressure of 0.57 MPa for pure MgH_2 at 350 ^0C. Therefore, a destabilizing effect of MgH_2 hydride phase due to the presence of fcc-Al takes place. XRD analysis showed after the process of dehydrogenation the presence of Mg (Al) solid solution and did not reveal Al and Mg-Al intermetallic compound. These facts testify that the presence or absence of the effect of MgH_2 or $Mg(Al)H_2$ hydride phase thermodynamic stability decrease depends on, among other things, the method and conditions of its obtaining.

There are works in which to reduce the decomposition temperature of MgH_2, obtained by reactive mechanical alloying (RMA) and to improve hydrogen desorption kinetics, its mechanical alloying by transition and nontransition metals [10-12,52,53,55,83-85] has been carried out. The authors [52] report about the effect of stoichiometric hydride MgH_2 formation enthalpy lowering and, consequently, the temperature of its decomposition to 210 ^0C due to the complex alloying of magnesium by Al, Ni, Ti at $Mg_{87}Ni_3Al_3Ti_7$ mechanical alloy synthesis by RMA method. Almost the same result of lowering the temperature of MgH_2 decomposition at the expense of magnesium alloying by Al, Ni, Mn was received in [53]. However, lower temperatures of MgH_2 decomposition of obtained mechanical alloys [52.53], as well as in [10-12,55,83-85], have been determined from thermogravimetric and DSK-curves (differential scanning calorimetry) obtained by MA samples heating in argon (not hydrogen). **Therefore, it is not clear whether they can be considered as temperatures of MgH_2 decomposition, which corresponds to the equilibrium hydrogen pressure of 0,1 MPa, and whether there will be a given in [52] the fact of a significant reduction in the temperature of MgH_2 hydride phase decomposition of mechanical alloy from 288 to 210 ^0C at hydrogen pressure in the reactor**

of 0,1 MPa? The answer to this question requires further investigations.

The most researchers continue searching only the ways to solve a task of kinetics of magnesium hydrogenation and MgH_2 dehydrogenation improvement [87-93]. The methods that permit to prevent the negative impact of the oxide/ hydroxide surface layer on dissociative chemisorption processes and hydrogen recombination and reduce the grain size for the reduction of its diffusion ways in the solid matrix are used. The processes of mechanical dispersion in the inert gas or hydrogen of MgH_2 commercial or Mg in the presence of different catalytic additives are mainly used. The influence of treated hydride on kinetic properties, the additives nature and mechanical activation treatment (MAT) are under investigation. When choosing alloying elements and additives to magnesium, their possible negative impact on the MA hydrogen capacity, reversibility of hydrogenation/ dehydrogenation process, the stability of the resulting nanostructures [94] should be taken into account. The impact of MgH_2 exposure in the air on its kinetic characteristics and dependence of the pointed impact on the magnesium hydride obtaining mode are under investigation [95, 96]. Its hould be noted that in [87-93] hydrogen desorption kinetics curves were obtained at MA samples heating in argon or in a vacuum. Unfortunately, this makes it impossible to compare the results of these studies with other experiments results obtained at isobaric heating of MA samples in hydrogen at a pressure of 0,1 MPa. Moreover, it does not allow to make conclusions regarding the hydrogen release rate from MA samples under normal pressure in the reactor, or higher than normal, that is, in terms of practical application of MA. A particular attention should be paid to a series of papers published in recent years [97-100], which reveal the opportunity to improve not only the sorption/desorption processes kinetics of hydrogen, but also lower the thermodynamic stability of magnesium hydride and its decomposition temperature, using indium or indium together with other metals (Al, Ti, Y) in magnesium solid solutions.

This article provides an overview and comparative analysis of the investigation results obtained by the authors. Experiments are aimed at the reduction of temperature and improvement of MgH_2 decomposition kinetics using the mechanical-chemical method of its obtaining, applying Ti, Fe, Ni, Al as alloying elements. The main attention is paid both to the role of each alloying elements and the role of the pair Al+Ti, Al+Fe, Al+Ni, Ti+Fe doping in reducing the temperature, improving the kinetics of hydride phase decomposition of MA, and to the methods and techniques search that allow to form complex of characteristics meeting the requirements for practical application of the hydrogen storage materials.

The peculiarity of this work is that the study of the hydrogen desorption process from synthesized MA is made exactly when the hydrogen pressure in the reactor is 0,1 MPa.

Experimental part

Materials and methods

To reduce the temperature, improve the kinetics of stoichiometric MgH_2 hydride decomposition, a range of new MA has been synthesized by reactive grinding in hydrogen of powders: pure Mg (further MA1); Mg + 10 wt. % Ti (MA2); Mg + 10 wt. % Fe (MA3); Mg + 10 wt. % Ni (MA4); Mg + 10 wt. % Al (MA5); Mg+10 wt.% Al +10 wt. % Ti (MA6); Mg + 10 wt. % Al + 10 wt. % Fe (MA7); Mg + 10 wt. % Al + 10 wt. % Ni (MA8); Mg + 3 at. % Al + 3at. % Ni + 7 at. % Ti (MA 9). **This alloy obtained by the same method (RMA) as used in [52, 55] was selected for verification. Therefore, at. %.** Another mechanical alloy-composite of Mg + 10 wt. % Fe + 10 wt. % Ti (MA 10) was received by milling of Mg, TiH_2, Fe powders mixture in argon.

The research task of this study was to obtain the above mentioned MA1 - MA10 mechanical alloys and explore the processes of hydrogen desorption from them of MgH_2 hydride phase (both immediately after mechanical synthesis and after the first hydrogenation/dehydrogenation cycles). Moreover, it was necessary to find out if the reduction of MgH_2 hydride phase formation enthalpy takes place and, consequently, the

equilibrium temperature decrease of its decomposition at a constant hydrogen pressure of 0,1 MPa due to the selected alloying elements and the obtained method. The selected alloying elements influence on MgH_2 decomposition kinetics was the aim of the investigatiopn as well.

The choice of Al as alloying elements was stipulatedby the fact that aluminum, having atomic radius less than of Mg (r_{Al} = 0.143 nm, r_{Mg} = 0.16 nm) and the enthalpy of its AlH_3 hydride formation is 36 kJ/mol compared to the enthalpy of MgH_2 hydride (74kJ/mol), can help reduce the latter (at magnesium alloying and aluminum in magnesium solid solution formation [9, 79]) and, consequently, reduce MgH_2 hydride phase decompositiontemperature of received mechanical alloys - composites. When choosing Ti, Fe, Ni, we proceeded from the fact that these transition metals have, as it is known, catalytic properties and at reactive mechanical synthesis, being dispersants, can substantially improve magnesium hydrogenation kinetics, and also, in accordance with theoretical prediction [9], significantly affect the thermodynamic stability of MgH_2 hydride phase created at the synthesis process.

In order to produce the MA1 – MA10 mechanicalalloys, thecommercialpowdersofMg, Ti, Fe, Ni, Al with a purity of 99.98 % and particles sizes of 100; 6,7; 10; 3; 100 μm, respectively, have been used as raw materials. Themechanical fusion by reactive grinding of

the mixture of powders of MA1-MA10 composition, was realized in a ball mill of the RETCH Firm with steel balls in a hydrogen atmosphere (under a hydrogen pressure of 1 MPa, for avelocity of rotation of 450 rot/min, duration of grinding of 10 h) for MA1-MA9 and in an argon atmosphere for MA10. The ratio of the metallic balls mass and the treated mixture of powders was 20:1. The equal conditions of all MA synthesis have been deliberately created, that allowed to compare the influence of different alloying elements on the temperature and hydride phase decomposition of synthesized MA. The same conditions of all MA syntheses have been deliberately provided, which allowed to make a proper comparison of different alloying elements effect on temperature and the kinetics of MgH_2 hydride phase decomposition of synthesized MA. All MA samples direct hydrogenation from the gas phase conditions. After synthesis MA samples were placed in a reactor and obtaining the first hydrogen desorption curve from its sample the latter was not removed from the reactor. At a temperature of 450 ^{0}C the reactor was filled with hydrogen until a hydrogen pressure was 3 MPa and at the sample cooling together with the furnace its first (and subsequent) hydrogenation from the gas phase took place.

Microstructures of the initial powder mixture and the synthesized composite alloys were studied using a Super-Probe 733 scanning electron microscope. The change of MA powders particle size after ten hours of RMA was evaluated by measuring powders specific surface by BET method. The measurement error did not exceed 10 %. For the X-ray phase diffraction analysis of specimens, we used a DRON-3M diffractometer. The X-Ray patterns were obtained in the CuKα - radiation with a graphite monochromator. The profiles of diffraction lines were plotted with scanning steps of 0.1° and holding at each point of the spectrum for 10–20 sec. The diffraction patterns were analyzed using fullprof software Powder Cell 2.4.

By the method of thermal desorption spectroscopy in a computerized automatic installation, we studied the influence of alloying elements on the hydrogen-sorption properties, thermal resistance, and the kinetics of hydrogen desorption from the MgH_2 hydride phase obtained by mechanical fusion. This installation made it possible to plot the isobars of resorption/desorption of hydrogen under various pressures (from 0.1 to 1.0 MPa) in the reactor and to perform the hydrogenation/dehydrogenation of specimens under pressures of up to 10 MPa and temperatures within the range from the room temperature to 1200 °C.

3. Results and discussion

The information on the phase structure and hydrogen storage capacity, i.e. the quantity of desorbed hydrogen by MA specimens

obtained by reactive mechanical alloying (RMA) and after the gas phase hydrogenation (GPH) is presented in Table 1. The table also

shows the average particle size of mechanical alloys powders (after RMA), which is calculated

Table 1. Phase'scompositionsandproperties of MA in the course ofitsfirst heating (after reactive mechanical alloying (RMA) and of its first hydrogenation from the gaseous phase (HGM)).

Mechanical alloy-composite (wt.%) MA9 in at. %	Phase's compositions		$D_{part.}$, μm	CapacityH$_2$ (wt.%)	
	RMA	HGM	RM A	RMA	HGM
MA1 (Mg)	Mg, MgH$_2$	Mg,MgH$_2$	0,7	5,1	6,3
MA2 (Mg + 10 Ti)	Mg, MgH$_2$, TiH$_2$, TiFe	MgH$_2$, TiH$_2$, TiFe	0,3	6,75	5,1
MA 3 (Mg + 10 Fe)	Mg,β-MgH$_2$, γ-MgH$_2$,MgO, Mg$_2$FeH$_6$, Fe	MgH$_2$, MgO,Fe	0,25	6,3	5,2
MA4 (Mg + 10 Ni)	Mg, MgH$_2$, Ni	Mg,MgH$_2$, Ni Mg$_2$NiH$_4$	0,4	4,6	6,8
MC 5 (Mg + 10 Al)	Mg, MgH$_2$, Mg$_2$Al$_3$	Mg, MgH$_2$, Mg$_2$Al$_3$	0,7	2,5	3,3
MA 6 (Mg + 10 Al +10 Ti)	Mg, MgH$_2$, Al, TiH$_2$, TiAl$_2$	MgH$_2$, Al, TiH$_2$, TiAl$_3$	0,47	6,56	5,6
MA 7 (Mg + 10 Al +10 Fe)	Mg, MgH$_2$, MgAl$_2$, Fe	Mg, MgH$_2$ FeAl$_2$,Al Mg$_2$FeH$_6$,	0,6	3,5	4,6
MA 8 (Mg + 10 Al +10 Ni)	Mg, MgH$_2$, Ni, Mg(AlH$_4$)$_2$	Mg, MgH$_2$, Ni, Mg$_2$Ni Mg(AlH$_4$)$_2$	0,47	3,0	5,5
MA 9 (Mg + 3Al +3 Ni + 7 Ti)	Mg, MgH$_2$, Ni, Mg$_2$NiH$_4$,TiH$_2$	did not do	0,5	5,4	6,2
MA 10 Mg + 10 Fe + 10 Ti	Mg, TiFe, TiFeH$_{2-x}$	MgH$_2$,TiH$_2$, Mg$_2$FeH$_6$, TiFeH$_{0,2}$, Fe	2,6	in Ar	4,9

based on obtained by low-temperature nitrogen adsorption BET (**Brunauer, Emmett and Teller)** of specific surface data.

As the table shows, all mechanical alloys (MA1-MA9) are composites, asa result of reactive mechanical alloying. They contain besides MgH$_2$hydride phase metallic Mg phase

(it indicates a partial Mg → MgH$_2$ transition for the same grinding time - 10 h for all MA), as well as new crystalline phases which are not parts of the initial mixture of mechanical alloys powders (except MA4) and are magnesium compounds with alloying elements or hydrides of such compounds, and in the case of MA2, they are TiH$_2$ and TiFe. After the first

hydrogenation-dehydrogenation cycles from the gas phase and in the case of MA3, MA4, MA7, MA8 changes in the composites phase composition have been taken place. Fig. 1shows MA7 specimen diffraction patterns after its synthesis by RMA method (Fig. 1a) and after
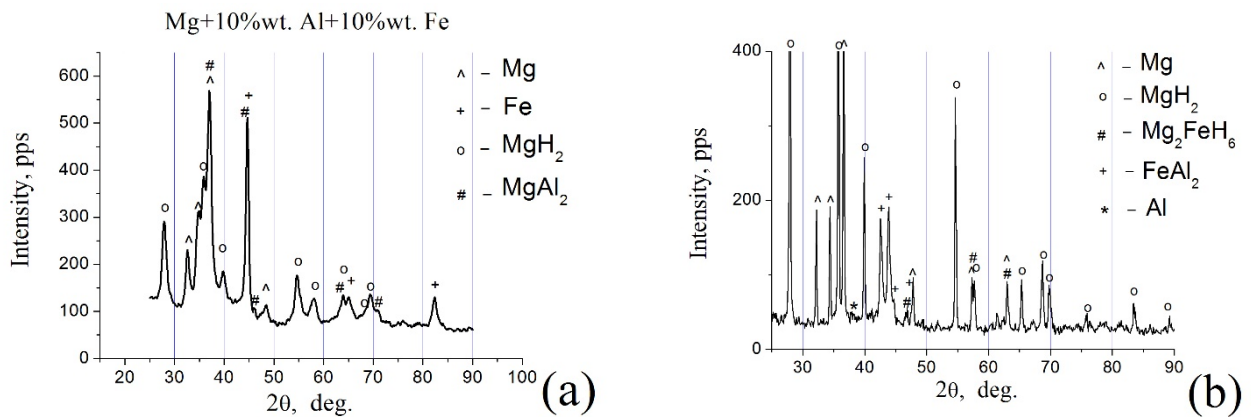

Figure 1. XRD pattern of the mechanical alloy MA7: (a) after its synthesis RMA and (b) after hydrogenation from gaseous phase in the 5th cycle.

hydrogenation from the gas phase in the 5th cycle (Fig. 1b). Thus, in the diffraction spectrum of MA7 after synthesis (Fig.1a) the diffraction reflexes of metallic magnesium and compound have been found out. Herewith, after hydrogenation from the gasphaseinthe5thcycle (Fig.1b) instead of $MgАl_2$ suchphasesasFeAl$_2$, $Mg_2FeH_6$and metallic aluminum appeared. In the case of mechanical MC1-MC9 alloys-composites the parameters of crystal lattices and

its hydride phase of MgH_2 with tetragonal structure as wel las reflexes of metallic iron and $MgAl_2$

volume of their unit cells both for β-MgH_2 hydride phase and for metallic Mg phase (when the quantity of the latter allowed to do it), have been determined by the full-profile Rietveld method using Powder Cell 2.4 program. The parameters of crystal lattices and volume of unit
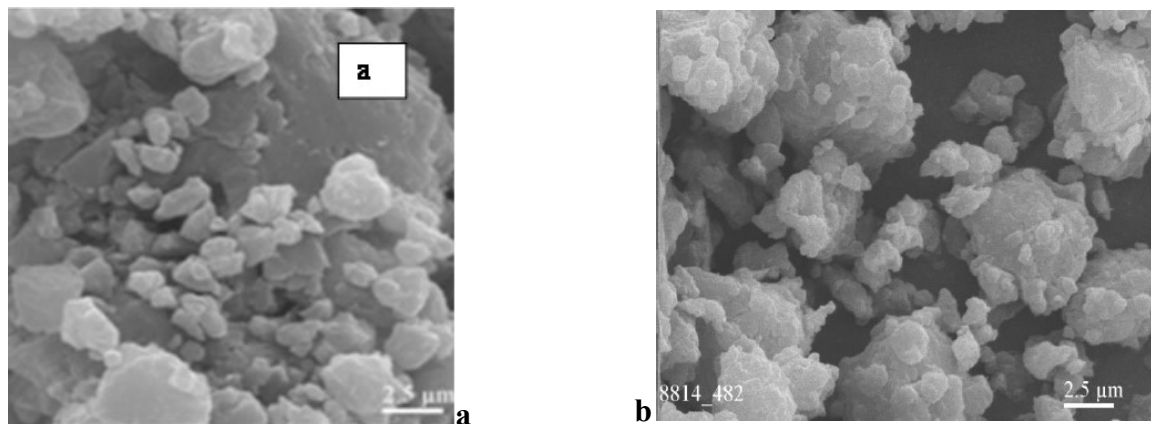

Figure 2. SEM images of powders of the mechanical alloy MA7: (a) - after its synthesis RMA, (b) - after hydrogenation from gaseous phase in the 5th cycle

cells of mentioned above MA are shown in Table 2.

The investigation of microstructure and morphology of obtained mechanical alloys powder particles have shown that as a result of a 10-hour grinding in hydrogen a significant powder particles dispersion of all MA powders is found out. After mechanical dispersion all MA powders have practically the same morphology, that is characterized mainly by the presence of a large number of rounded particles ranging from 0.1 to 0.5 μm and a small portion of large size sinters (from 1 to 8 μm). Based on the experimental data for specific surface area, average particle size of all MA powders ranges of 0.2 - 0.5 μm (see Table 1). Fig. 2 shows (as an example) MA7 microstructure after synthesis by RMA method (Fig. 2 a) and after 5 cycles of hydrogenation from the gas phase (Fig. 2b). It should be noted that after repeated MA powders hydrogenation-dehydrogenation from the gas phase, the powders average particle size

Table 2. Crystal structure data (unit cell parameters: a, c - Å; V - Å^3) for β-MgH$_2$ hydride phase and Mg phase of composites

Mechanical alloy-composite	Phase			
	Mg		MgH$_2$	
	after RMA	after HGM	afterRMA	after HGM
MA1	a = 3,2088 c = 5,2077 V= 46,437	-	a = 4,5160 c = 3,0240 V= 61,672	a=4,5167 c=3,0245 V=61,686
MA2 (Mg + 10 wt.% Ti)	–	a =3,2123 c =5,2022 V= 46,489	a = 4,5042 c = 3,0137 V= 61,141	a =4,5150 c = 3,0161 V= 61,484
MA 3 (Mg + 10 wt.% Fe)	–	–	a = 4,5089 c = 3,0130 V= 61,2557	a =4,5208 c = 3,0237 V= 61,787
MA4 (Mg + 10 wt.% Ni)	a = 3,2074 c = 5,1980 V= 46,310	–	a = 4,5223 c = 3,0157 V= 61,675	a = 4,5188 c = 3,0212 V= 61,692
MA5 (Mg + 10 wt.% Al)	a = 3,1777 c = 5,1702 V= 45,213	a = 3,1887 c = 5,1812 V= 45,624	a = 4,5198 c = 3,0005 V= 61,296	a = 4,5281 c = 3,0016 V= 61,544
MA 6 (Mg + 10 wt.% Al +10 wt.% Ti)	–	–	a = 4,5034 c = 3,0091 V= 61,026	a = 4,5185 c = 3,0215 V= 61,689
MA 7 (Mg + 10 wt.% Al +10 wt.% Fe)	a = 3,1750 c = 5,16767 V= 45,114	a = 3,2099 c = 5,2125 V= 46,512	a = 4,5120 c = 3,0100 V= 61,278	a = 4,5100 c = 3,0320 V= 61,671
MA 8 (Mg + 10 wt.% Al +10 wt.% Ni)	a = 3,2051 c = 5,1989 V= 46,252	–	a = 4,5243 c = 3,0248 V= 61,916	–

MA 9 (Mg + 3 at.% Al +3 at.% Ni+ 7 at.%Ti)	a = 3,1702 c = 5,1101 V= 44,474	–	a = 4,5139 c = 3,0227 V= 61,588	–

decreases as a rule, and the average grain size increases due to cyclical heating-cooling. The confirmation to this can be found, if compare the MA7 specimen width of diffraction reflections before and after cycling shown in Fig. 1a and Fig. 1b: in the last case, you can watch them marked narrowing.

Table 3. Hydrogen desorption from MA in the course of its first heating after mechanochemical synthesis (RMA) and of its first hydrogenation from the gaseous phase (HGM)

Sample	1-st desorption after RMA		1-st desorption after HGM	
	$T_{st},^0C$	$T_{max},^0C$	$T_{st},^0C$	$T_{max},^0C$
MA1 (Mg without additives)	315	430	300	385
MA2 (Mg + 10 wt.% Ti)	260	360	300	317
MA 3 (Mg + 10 wt.% Fe)	260	320	300	317
MA4 (Mg + 10 wt.% Ni)	300	330	290	315
MA5 (Mg + 10 wt.% Al)	310	445	310	360
MA 6 (Mg + 10 wt.% Al +10 wt.% Ti)	288	330	275	318
MA 7 (Mg + 10 wt.% Al +10 wt.% Fe)	250	368	288	368
MA 8 (Mg + 10 wt.% Al +10 wt.% Ni)	310	410	350	410
MA 9 (Mg + 3at.% Al +3at.% Ni+ 7at. %Ti)	280	355	280	318
MA 10 (Mg + 10 wt.% Fe +10 wt.% Ti)	-	-	220	318

3.1 Thermal stability of Mg – Me (Me: Ti, Fe, Ni, Al) and Mg – Me₁ – Me₂ (Me₁= Al; Me₂=Ti, Fe, Ni) mechanical alloys-composites

MA1-MA5 samples hydrogen desorption isobars at their first heating after RMA synthesis are shown in Fig. 3, and after their first hydrogenation from the gas phase - in Fig. 4. It should be paid attention to the conditions of their production - all isobars were obtained at constant pressure of hydrogen in the reactor (0,1 MPa) and sample heating rate of 3 °C/min. Theisobarsshown in Fig. 3 and 4 were used to determine both the hydrogen desorption beginning temperature **($T_{st.}$)** from hydride phase MgH_2 of MA1-MA5 and temperature **T_{max}**, that corresponds to the maximum speed of hydrogen release. The obtained data are shown in Table 3, which shows that the temperature of MA1 hydrogen desorption beginning from the MgH_2hydride phase afterRMA synthesis is 315^0C. Additive to magnesium of each alloying elements (Ti, Fe, Ni, Al) leads to its decline: itis maximal for Ti and Fe (55 deg.) and minimal in the case of Al (5 deg.). $T_{st.}$ reducing for MA2

and MA3 from 315 to 260 ^{0}C shows that the addition of Ti and Fe leads to a significant MA2 and MA3 mechanical alloys thermal stability decreasing.

As the temperature of 260 ^{0}C is lower [86] than 288 ^{0}C (the temperature of MgH_2 decomposition at the equilibrium pressure of 0.1 MPa) the question is whether MgH_2 hydride phase thermodynamic stability decrease takes place because of its alloying by iron and titanium. A very slow hydrogen desorbtion process kinetics from MA2 and MA3 at 260 ^{0}C and presence of other hydride phases besides MgH_2 in MA2 and MA3, (Table1:TiH_2, Mg_2FeH_6) does not allow to give a definite answer to this question and requires further research. From the analysis of the curves of the first hydrogen desorption after synthesis from MA2 – MA5 (Fig. 3), it was found that as the result of reactive milling during 10 h of magnesium mixtures with the addition of 10 wt. % of Ti, Fe, Ni and Al, hydrogen capacities of 6,75 wt. %, 6,3 wt. %, 4,6 wt. % and 2,5 wt. %, respectively, can be achieved. A lower value of hydrogen capacity in the case of Ni additive to magnesium comparing to the case of Ti and Fe additives, is explained by the fact that 10-hour grinding was not sufficient to achieve maximum hydrogen capacity.

Analyzing and comparing the results of hydrogen desorption process from MgH_2 hydride phase of MC2 –MC5 mechanical alloys immediately after their RMA synthesis and after the next cyclic hydrogenation from gas phase (Table 3) one can see that the temperatures of T_{st} and T_{max} do not remain unchanged. The effect of lowering the temperature of hydrogen desorption beginning from 315 to 260 ^{0}C caused by Ti and Fe alloying (compared to received unalloyed MgH_2 MA1 hydride phase obtained by the same RMA) is significantly lower: T_{st} increased from 260 ^{0}C to 300 ^{0}C for MA2 and MA3. The lowest temperature of hydrogen desorption beginning after hydrogenation from gas phase revealed MA4. Thus, the results obtained, point to the importance of the mechanical alloys properties investigation and their mechanical characteristics assessment, not only after their RMA synthesis but also after the first hydrogenation/dehydrogenation cycles to define the fields of their application.

To evaluate the influence of complex alloying by Ti, Fe, Ni and by nontransition metal Al on decomposition temperature and thermal stability of MgH_2 phase hydrogen desorption from MA6-MA10 have been studied. Hydrogen desorption isobars obtained at the first heating after RMA synthesis of MA6-MA9 samples are shown in Fig. 5. After the first hydrogenation fromthe gas phase of MA6-MA10 are in Fig. 6. Likein the previous case of MA1-MA5 alloys-composites all isobars were obtained at sample heating rate of 3 ^{0}/min and $T_{st.}$ and T_{max} temperature values for MA6-MA10 are presented in Table 3. From the hydrogen thermal desorption curves shown in Fig. 5 and

Table 3 one can see that in the case of MA7 composite the adding of 10 wt. % Al + 10 wt. % Fe to magnesium led to a decrease in temperature of hydrogen desorption beginning from 315 to 250 ^{0}C. Such desorption temperature reduction is the largest, when
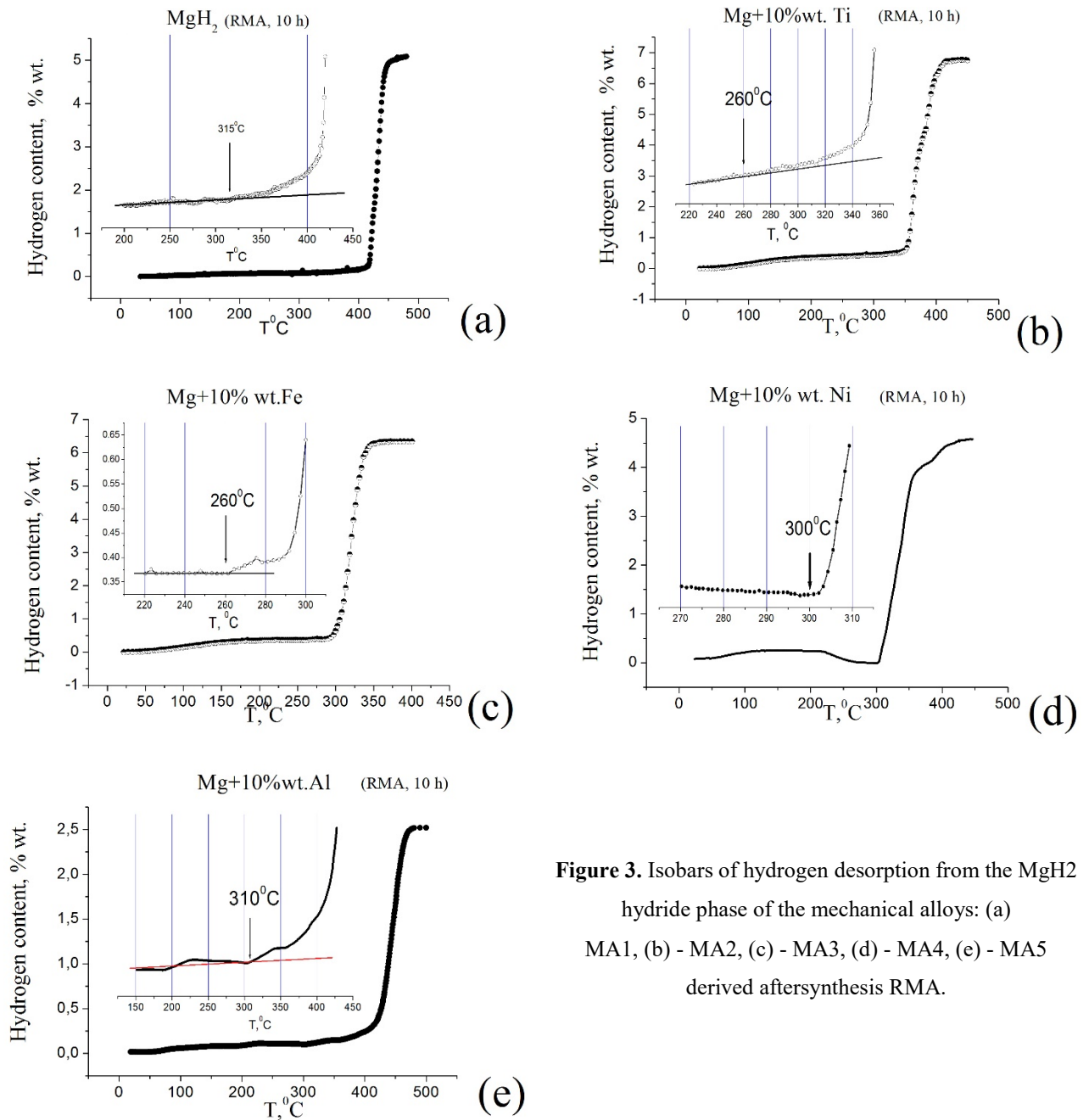
(a)

(b)

(c)

(d)

(e)

Figure 3. Isobars of hydrogen desorption from the MgH2 hydride phase of the mechanical alloys: (a) MA1, (b) - MA2, (c) - MA3, (d) - MA4, (e) - MA5 derived aftersynthesis RMA.

compared with the addition of 10 wt. %Al +10% wt.% Ti and 10 wt.% Al + 10 wt.% Ni to magnesium for MA6 and MA8. It points to lowering of MgH$_2$ thermodynamic stability as the temperature of 250 ^{0}C is lower than the temperature of 288 ^{0}C, which according to [86] corresponds to equilibrium hydrogen pressure of 0.1 MPa. The indicated temperature decrease should be attributed, in our opinion, to the formation of Mg(Fe,Al)H$_x$ hydride of iron and aluminum solid solution in magnesium, at mechanical activation synthesis processes,

which, in accordance with the theoretical prediction [9], should have a lower thermodynamic stability than magnesium hydride MgH_2. A rather noticeable decrease (because of Fe and Al adding) in unit cell volume of β-MgH_2 hydride phase (alloy MA7)
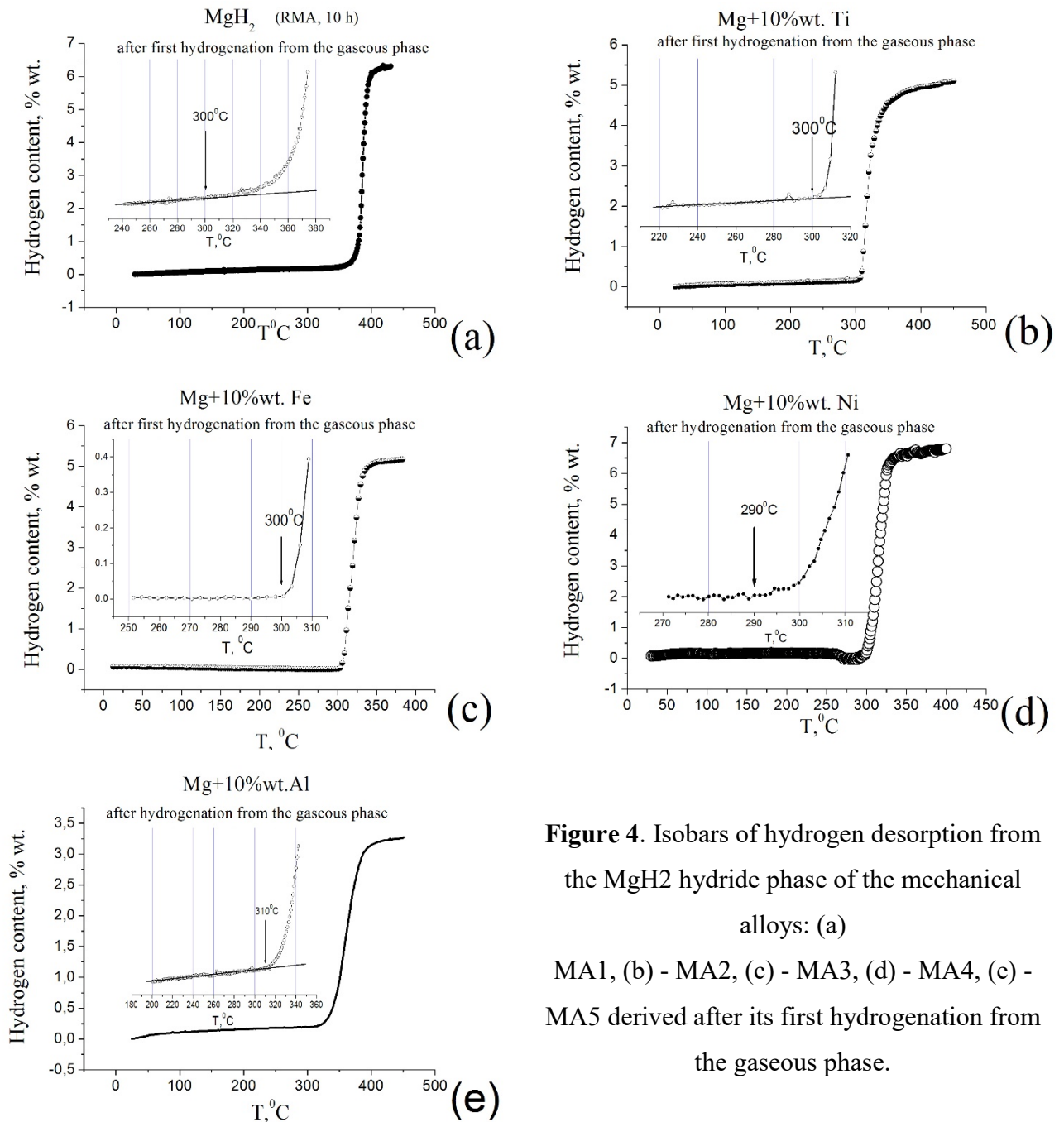

Figure 4. Isobars of hydrogen desorption from the MgH2 hydride phase of the mechanical alloys: (a) MA1, (b) - MA2, (c) - MA3, (d) - MA4, (e) - MA5 derived after its first hydrogenation from the gaseous phase.

compared with the unit cell volume of the same hydride phase without alloying elements (mechanical alloy MC1) testifies the formation of $Mg(Fe,Al)H_x$ solid solution: from V = $6,1672 \cdot 10^{-2}$, nm^3 for MA1 to V = $6,1278 \cdot 10^{-2}$, nm^3 for MA7 (see Table 2).Even more convincing evidence of the possible formation of iron and aluminum solidsolutionin magnesium at the synthesis may be themetallicMgphase unit cell volume reduction

of MA7 mechanical alloy compared with that one for MA1 mechanicalalloy: from V $=4{,}6437 \cdot 10^{-2}$, $nm^3$for MA1 to for MA7. If we pay attention to the fact that measured by us

hydrogen desorption beginning temperature from MgH_2 hydride phase of MA3 (Mg + 10 wt.% Fe) mechanical alloy was about
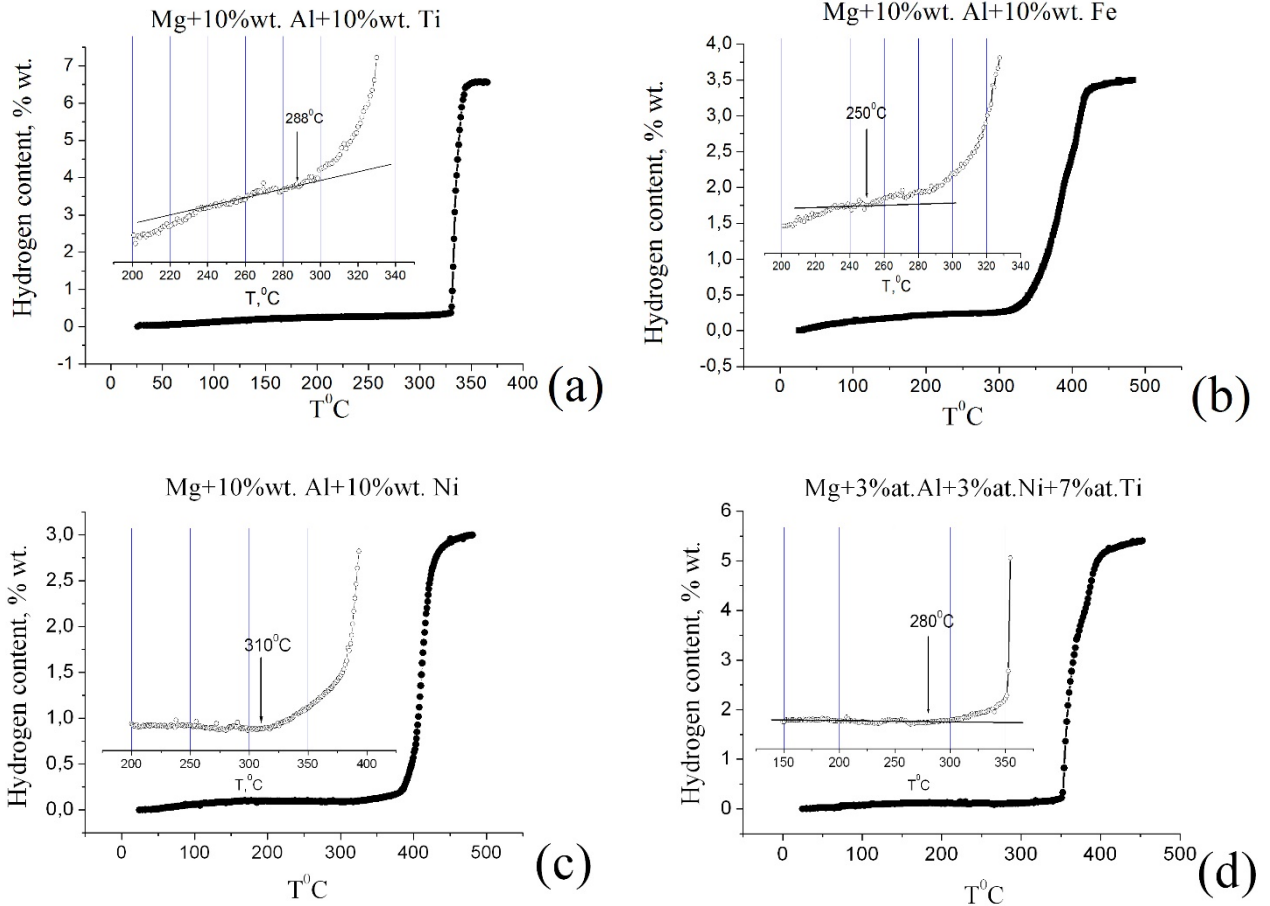

Figure 5. Isobars of hydrogen desorption from the MgH2 hydride phase of the mechanical alloys: MC6-(a), MC7-(b), MC8-(c), MC9-(d) derived aftersynthesis RMA.

260^0C, while in the case of MA5 (Mg +10 wt.% Al) mechanical alloy it was 310 ^{0}C, it would be a logical assumption that iron played a major role in 65 degree decrease of hydrogen hydride beginning temperature of β-MgH_2 hydride phase of MA7 mechanical alloy.It should be noted that under the same synthesis conditions of MA6-MA9 by RMA, the lowering of thermodynamic stability and, consequently, the reduction in the temperature of hydride phase MgH2 decomposition of mechanical alloy at hydrogen

pressure of 0.1 MPa in the reactor, could be achieved only for MA7.

From the curve of hydrogen desorption of MA7 after the first hydrogenation from the gas phase we can see that the temperature of hydrogen desorption beginning is about 288 ^{0}C (Fig. 6). This temperature is already higher than the temperature of 250 ^{0}C, specified in the previous hydrogen desorption (first) from MA7 investigation after its synthesis and contact with air, and coincides with a temperature of

stoichiometric MgH_2 decomposition at the equilibrium hydrogen pressure of 0,1 MPa in the reactor [86]. The fact of increasingof hydrogen desorption beginning temperature

from 250 ^0C to 288 ^0C may indicate that as a result of hydrogenation from gas phase of MA7 mechanical alloy under the above conditions instead of hydride of $Mg(Fe,Al)H_x$ solid
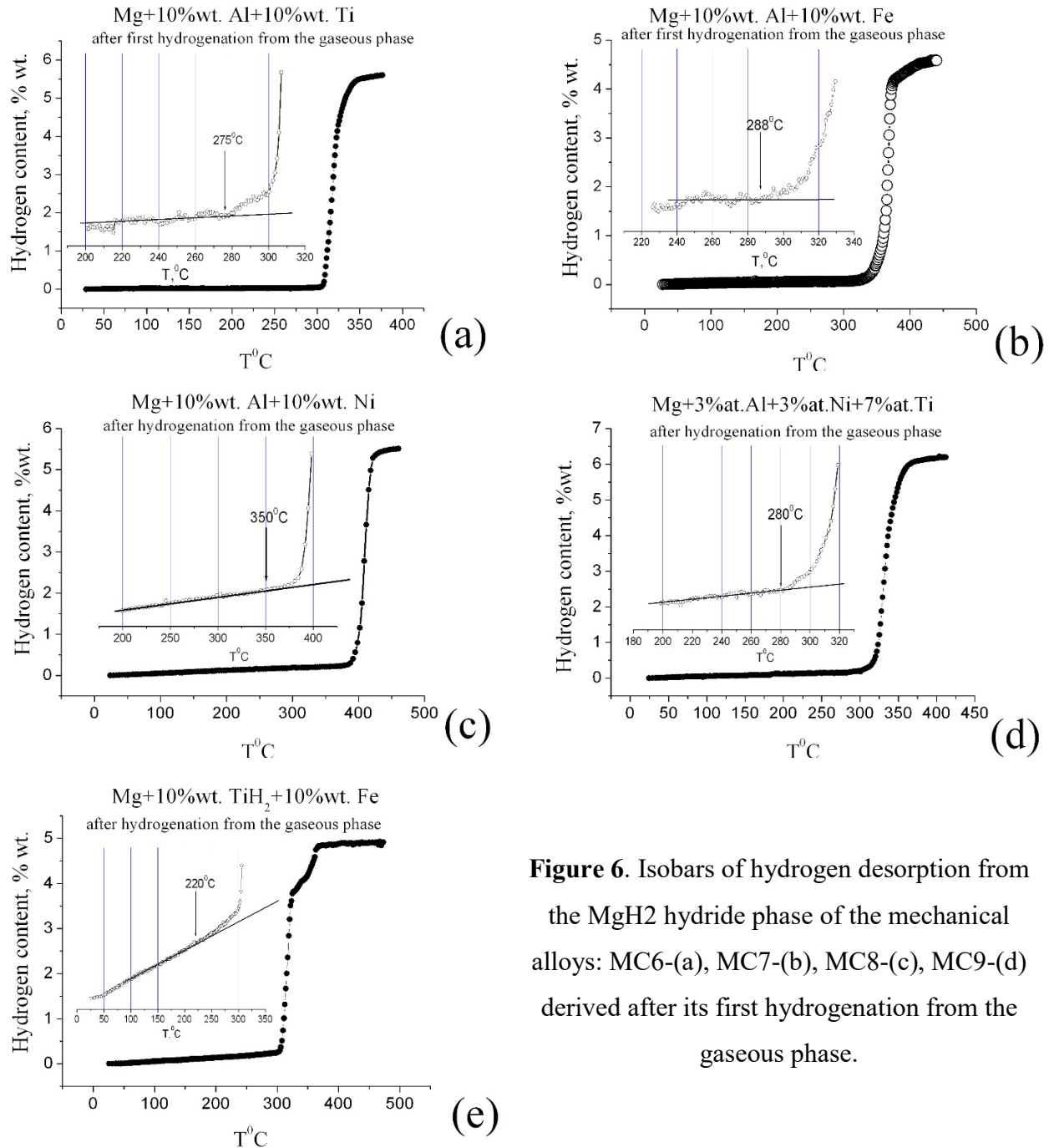

Figure 6. Isobars of hydrogen desorption from the MgH2 hydride phase of the mechanical alloys: MC6-(a), MC7-(b), MC8-(c), MC9-(d) derived after its first hydrogenation from the gaseous phase.

solution a hydride phase which corresponds to stoichiometric MgH_2 magnesium hydride is formed. So we can state that at the cyclic hydrogenation from gas phase of MA7 sample

the effect of thermodynamic stability decrease of its MgH_2 hydride phase, which we observed in the study of the first of hydrogen desorption from MA7 after its synthesis is not preserved.

This may be because of Fe and Al solid solution in magnesium decomposition at heating of MA7 sample in the process of its hydrogenation from the gas phase with the formation such phases as FeAl$_2$, Mg$_2$FeH$_6$ and metallic aluminum (Table 1). An increase in the unit cell volume of MgH$_2$hydride phase of MA7 mechanical alloy after its hydrogenation from the gas phase in the fifth cycle from V = 61,278 Å^3, to V=61,671 Å^3 can be this assumption confirmation, as well (Table 2).

The temperature of hydrogen desorption beginning (T$_{st}$) from MA10 (Mg+10 wt.% Fe +10 wt. % Ti) mechanicalalloy, which was obtained by grinding in argon with the following hydrogenation from the gas phase was 220 ^{0}C (*i.e.* more lower than T$_{st.}$ for MA7 250 ^{0}C). However, this quite low value of T$_{st.}$ (220 ^{0}C) is not evidence of MgH$_2$ MA10 hydride phase thermodynamic stability decreasing. Hydrogen desorption from MA10 that begins at temperature of 220 ^{0}C is the result of decomposition beginning at this temperature of TiFeH$_{0,2}$ hydride phase and possibly TiFeH$_{2-x}$ phase, but not, as expected, Mg(Ti, Fe)H$_2$ hydride phase alloyed by titanium and iron. It should be noted that given in Table 1 values of hydrogen capacity of MA6-MA10 were obtained under the same conditions both for the RMA synthesis and hydrogenation from the gas phase of pointed MA, and do not correspond to the maximum values of the hydrogen capacity, which can be achieved by increasing the grinding duration or hydrogenation time from the gas phase.It firstly concerns of MA7, which value of hydrogen capacity is 3.5 wt. % and substantially differs, for example, from those for MA6 (6,56 wt. %) and MA9 (5.4 wt. %). Obviously, 10 h of reactive grinding for MA7 is not enough to achieve the maximal possible capacity.

3.2 Mg – Me (Me=Ti, Fe, Ni, Al) and Mg – Me$_1$ – Me$_2$ (Me$_1$=Al; Me$_2$=Ti, Fe, Ni) mechanical alloys-composites hydrogen desorption kinetics process

Hydrogen desorption kinetics from β-MgH$_2$ hydride phase of all MA synthesized by us after their hydrogenation from the gas phase under the same conditions has been investigated at the following temperatures: 300 ^{0}C for MA2-MA5, MA9, MA10 and 320, and 400 ^{0}C for MA1, MA6-MA8. Hydrogen desorption kinetic curves are presented in Fig. 7. All the curves presented in this figure were obtained at a constant hydrogen pressure of 0,1 MPa in the reactor. The data of hydrogen time release of half of hydrogen quantity (τ$_{1/2}$) and total hydrogen quantity release (τ$_t$) for all MAs are shown in Table 4. As we can see from Table 4 and kinetic curves obtained at 300 ^{0}C (Fig.7a), MA4 and MA10 mechanical alloys-composites have the best kinetics of hydrogen desorption from MgH$_2$, for which τ$_{1/2}$ is 7 and 7,5 min, respectively, and τ$_t$ - 14 and 16 min. We can see (Table 4), as well, that the time τ$_{1/2}$increases in the row: MA3, MA2, MA9,

MA5: 13; 16,5; 22; 58 min. If compare the $\tau_{1/2}$ values with the time of MA1release (at a higher temperature of 320 ^{0}C) half of the hydrogen

from MgH$_2$ hydride phase, which is 71 min, it can be concluded that additives of Ni, Fe, Ti to magnesium improve the
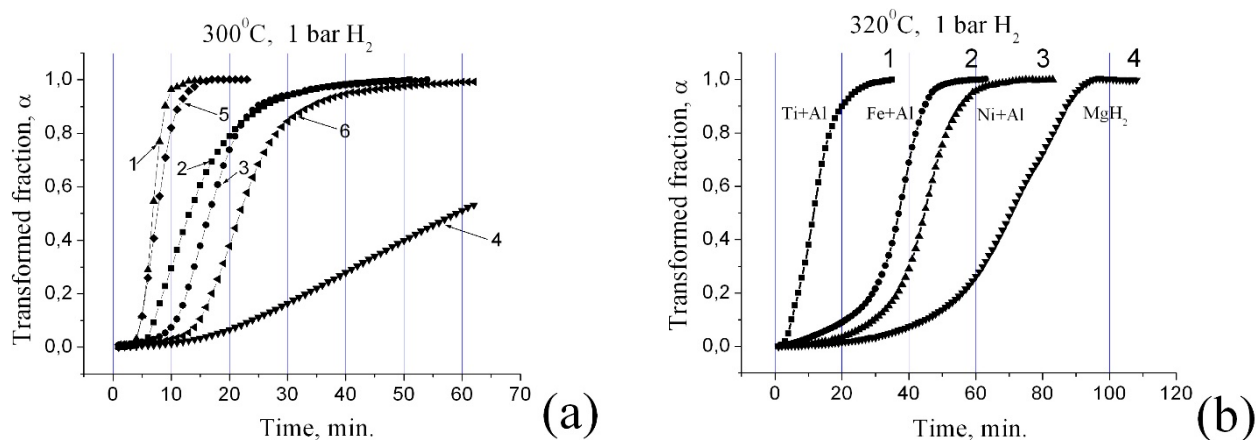

Figure 7. Kinetic curves of isothermal hydrogen desorption from the MgH2 hydride phase of the mechanical alloys: curve 1- MA2, curve 2 - MC3, curve 3 - MC4, curve 4 - MC5, curve 5 - MC9, curve 6 - MC10 at constant hydrogen pressure of 0.1 MPa in the reactor and temperature (a) 300 ^{0}C and (b) 320 ^{0}C.

MA hydrogen desorption process kinetics from β-MgH$_2$hydride phase.

Fig. 7 b presents the kinetic curves of hydrogen desorption at a temperature of 320 ^{0}C from MA6, MA7, MA8 mechanical alloys-composites and MA1, to be compared. The data of their $\tau_{1/2}$ and τ_t are shown in Table 4. The best MA hydrogen desorption kinetics from MgH$_2$ hydride phaser evealed MA6 composite for which $\tau_{1/2}$ is 11.5 and τ_t - 30 min. Herewith, the main part in kinetics improvement, as it was found, plays titanium but not aluminum. It is known that titanium, as well as other transition metals, has catalytic properties and helps to reduce MA powder particles of carbon and oxygen-containing groups adsorbed on the surface, which, as shown by XPS studies [65],

can block the catalytic centers and control both the hydrogen dissociative chemisorption at hydrogenation and the process of recombination at dehydrogenation.

We can assess the influence of various additives of alloying elements on the kinetics of hydrogen desorption from MA by analyzing temperatures T_{max} shown in Table 3, which correspond to the maximum speed of hydrogen release from a given MA and, as a rule, correlate with the value of$\tau_{1/2}$ of the same MA. The pointed correlation takes place for MA2, MA3, MA4 when Ti, Fe, Ni are added to magnesium, and it is very clear for MA6, MA7, MA8 when additives are Al + Ti, Al + Fe, Al + Ni. The lowest T_{max} value for MA6 in comparison with MA7 and MA8 shows the

greatest influence of simultaneous alloying by aluminum and titanium on the dissociation kinetics of β-MgH_2 hydride phase.

Table 4. Time (min.) of desorption half ($\tau_{1/2}$) and full (τ_f) hydrogen amount from MgH_2 hydride phase at 300 ^{0}C, 320^{0}C, 400 ^{0}C

Sample	300 ^{0}C		320 ^{0}C		400 ^{0}C	
	$\tau_{1/2}$	τ_f	$\tau_{1/2}$	τ_f	$\tau_{1/2}$	τ_f
MA1 (Mg)	88	130	71	95	6,5	11
MA2 (Mg + 10 wt.% Ti)	16,5	50				
MA 3 (Mg + 10 wt.% Fe)	13	50				
MA4 (Mg + 10 wt.% Ni)	7	14				
MA5 (Mg + 10 wt.% Al)	58	175			6,5	20
MA 6 (Mg + 10 wt.% Al +10 wt.% Ti)			11,5	30	3,5	12
MA 7 (Mg + 10 wt.% Al +10 wt.% Fe)			37	55	5,5	12
MA 8 (Mg + 10 wt.% Al +10 wt.% Ni)			44,5	73	3,5	9
MA 9 (Mg + 3at.% Al +3at.% Ni+ 7at. %Ti)	22	60				
MA 10 (Mg + 10 wt.% Fe +10 wt.% Ti)	7,5	16				

It should be noted that the mode and conditions of MgH_2 hydride obtaining significantly affect the kinetics of hydrogen desorption from it and, most notably, this effect appears at low temperatures. As established in [96], with increasing the grinding time from 10 to 20 hours $\tau_{1/2}$-for MA1 sample at 330 ^{0}C and hydrogen pressure of 0,1 MPa is reduced from 55 to 31 min, *i.e.* there is a significant improvement of hydrogen desorption kinetics from MgH_2. The same improvement of kinetic characteristics in case of grinding time increase should be expected almost for all investigated mechanical alloys-composites, for which to make a correct data comparison, was chosen the same grinding time of 10 h. But the latter was not enough to achieve the maximum MA powders disintegration, and thus, to reduce hydrogen diffusion paths and, consequently, to improve the hydrogen desorption kinetics from MgH_2 hydride phase of mechanical alloy-composites.

Conclusion

It was established that: by reactive grinding during 10 h of magnesium with the additives of 10 wt. % Ti, Fe, Ni and Al the hydrogen capacity of 6,75 wt.%; 6,3 wt.%; 4,6 wt. % and 2,5 wt. % can be achieved, respectively.

Ni, Fe, Ti transition metals additives to magnesium significantly improve hydrogen desorption kinetics process of MgH_2 hydride phase. The best kinetics of hydrogen desorption at pressure of 0,1MPa in the reactor and a temperature of 300 ^{0}C had MA4 and MA10 alloys-composites. 10 wt.% Al +10 wt.% Fe addition to magnesium at using of RMA leads to a decrease in temperature of hydrogen desorption to 250 ^{0}C, *i.e.* 65 ^{0}C lower, and points to lowering of MgH_2 thermodynamic

stability, which took place due to the formation of Al and Fe in magnesium (Mg(Fe,Al)H$_2$) solid solution. At the following cyclical hydrogenation from gas phase of MA7 mechanical alloy the above mentioned effect of thermodynamic stability reducing of MgH$_2$ is not observed.

Synthesized by RMA Mg-based mechanical alloys-composites with additives of Ni, Fe, Ti can accumulate of 5-6,5 wt.% of hydrogen. The MgH$_2$ hydride phase with low thermalstability and improved kinetics of its decomposition and exploitation characteristics of these composite materials concerning of hydrogen storage make it possible to use themat stationary application conditions.

Conflict of interest

The authors confirm that this article content has no conflictof interest.

References

[1] J. Huot, G. Liang and R. Schulz, "Mechanically alloyed metal hydride systems,Structure of nanocomposite metal hydrides",Appl. Phys., Vol. A 72, pp. 187-195, 2001.

[2] G. Liang, J. Huot andS. Boily, "Catalytic effect of transition metals on hydrogen sorption in nanocrystalline ball milled MgH$_2$ – Tm (TM=Ti,V,Mn,Fe,Ni) systems", J. Alloys Compd., Vol. 292, pp. 247-252, 1999.

[3] J. Huot, J.F. Pelletier, G. Liang, M. Sutton and R. Schulz, "Structure of nanocomposite metal hydrides", J. Alloys Compd., Vol. 330-332, pp. 727-731, 2002.

[4] W. Oelerich, T. Klassen and R. Borman, "Metal oxides as catalysts for improved hydrogen sorption in nanocrystalline Mg-based materials", J. Alloys Compd., No315, pp. 237-242, 2001.

[5] Z. Degouche, J. Goyette, T.K. Bose and R. Schulz, "Moisture effect on hydrogen storage properties of nanostructured MgH$_2$ –V-Ti composite", J. Hydrogen Energy, Vol. 28, pp. 983-988, 2003.

[6] J. Huot, J.F. Pelletier, L.B. Lurio., M. Sutton and R. Schulz, "Investigation of degydrogenation mechanism of MgH$_2$–Nb nanocomposites",J. Alloys Compd., Vol. 348, pp. 319-324, 2003.

[7] G. Barkhordarian, T. Klassen and R. Borman, "Fast hydrogen sorption kinetics of nanocrystalline Mg using Nb$_2$O$_5$ as catalyst", Scripta Materialia, No 49, pp. 213-217, 2003.

[8] Q. Li., Q. Lin, K.C. Chou, Li. Jiang and F. Zhan, "Hydrogen storage properties of mechanically alloyd Mg-8 mol% LaNi$_{0,5}$ composite", Materials Research Society, Vol.19, pp. 2871-2876, 2004.

[9] C.X. Shang, M. Bououdina, Y. Song and Z.X. Guo, " Mechanical alloying and electronic simulation of (MgH$_2$ + M) system (M= Al, Ti, Fe, Ni, Cu and Nb) for hydrogen storage", J. Hydrogen Energy, Vol. 29, pp. 73-80, 2004.

[10] A. Bassetti, E. Bonetti, L. Pasquini, A. Montone, J. Grbovic and V. Antisari, "Hydrogen desorption from ball milled MgH$_2$ catalysed with Fe", Eur. Phys., Vol.B 43, pp. 19-27, 2005.

[11] S. Deledda, A. Borissova and C. Poinsignonon, "H-sorption in MgH$_2$ nanocomposites containing Fe or Ni with fluorine", J. Alloys Compd., Vol. 404-406, pp. 409-412, 2005.

[12] N. Hanada, T. Ichikawa and H. Fujii, "Catalytic effect of Ni nano-particle and Nb oxide on H-desorption properties in MgH$_2$ prepared by ball milling", J.Alloys Compd., No 404-406, pp. 716-719, 2005.

[13] A. Borgschulte, J.H. Rector and B. Dam, "The role of niobium oxide as a surface catalyst for hydrogen absorption", Catalysis, Vol. 235, pp. 353-358, 2005.

[14] P.-A Hugg, M. Dornheim and T. Klassen, "Thermal stability of nanocrystalline magnesium for

hydrogen storage", J. Alloys Compd., No 404-406, pp. 499-502, 2005.

[15] K.-F. Aguey-Zinsou, J.R. Ares- Fernandes and T. Klassen, "Using MgO to improve the (de)hydriding properties of magnesium", Mater. Res. Bull., Vol. 412, pp. 1118-1126, 2006.

[16] P. Delchev, T. Himitliiska and T. Spassov, "Microstructure and hydriding properties of ball-milled Mg-10 at.% MmNi$_5$ (Mm=La, Ce-rich mischmetal) composites", J. Alloys Compd., Vol. 417, pp. 85-91, 2006.

[17] E. David, "Nanocrystalline magnesium andits properties of hydrogen sorption", Achievements in Materials and Manufacturing Engineering,Vol. 20, pp. 87-90, 2007.

[18] S.-Ah Jin., S. Jae-Hyeok, A. Jae-Pyoung, C. Young Whan and Y. Kyung-Woo, "Improvement in hydrogen sorption kinetics of MgH$_2$ with Nb hydride catalyst", Acta Materials, vol. 55, pp. 5073-5079, 2007.

[19] L. Xie, Y. Liu, Y.T. Wang, J. Zheng and X.G. Li, "Superior hydrogen storage kinetics of MgH$_2$ nanoparticles doped with TiF$_3$", Acta Materials, Vol. 55, pp. 4585-4591, 2007.

[20] H.Imamura, K.Yoshihara, M. Yoo, I.Kitazawa, Y. Sakata and S. Oshima, "Dehydriding of Sn/MgH$_2$ nanocomposite formed by ball milling of MgH$_2$ with Sn", J. Hydrogen Energy, Vol. 32, pp. 4191- 4194, 2007.

[21] R.A. Varin, T. Czujko, E.B. Wasmund and Z.S. Wronski, "Hydrogen desorption properties of MgH$_2$ nanocomposites with nano-oxides and inco micrometric and nanometric – NiT", J. Alloys Compd, Vol. 446-447, pp. 63-65, 2007.

[22] V.D. Dobrovolsky, O.G.Ershova, Y.M. Solonin, O.Y. Khyzhun and V. Paul-Boncour, "The influence of TiB$_2$ upon thermal stability of a hydride phase of the Mg-based mechanical alloy", J. Alloys Compd., Vol. 465, pp. 177-182, 2008.

[23] M. Polanski and J. Bystrzycki, "Comparative studies of the influence of different nano-sized metal oxides on the hydrogen sorption properties of magnesium hydride", J. Alloys Compd., Vol. 486, pp. 697-701, 2009.

[24] A. Patah, A. Takasaki and J.S. Szmyd, "Influence of multiple oxide (Cr$_2$O$_3$/Nb$_2$O$_5$) addition on the sorption kinetics of MgH$_2$", J. Hydrogen Energy, Vol. 34, pp. 3032-3037, 2009.

[25] L.P. Ma, X.D. Kang, H.B. Dai, Y. Liang, Z.Z. Fang P.J. Wang, P. Wang and H.M. Cheng, "Superior catalytic effect of TiF$_3$ over TiCl$_3$ in improving the hydrogenn sorption kinetics of MgH$_2$: Catalytic role of fluorine anion", Acta Materials, Vol. 57, pp. 2250-2258, 2009.

[26] L. Xie, Y. Liu and X. Zhang, "Catalytic effect of Ni nanoparticles on the desorption kinetics of MgH$_2$ nanoparticles", J. Alloys Compd., Vol. 482, pp. 388-392, 2009.

[27] R.A. Varin, T. Czujko and Z.S. Wronski, "Thermal stability of Vale Inco nanometric nickel as a catalytic additive for magnesium hydride (MgH$_2$)", J. Hydrogen Energy, Vol. 34, pp. 8603-8610, 2009.

[28] H.Imamura, K. Tanaka and I.Kitazawa, "Hydrogen storage properties of nanocrystalline MgH$_2$ and MgH$_2$/Sn nanocomposite synthesized by ball milling", J. Alloys Compd., vol. 484, pp. 939-942, 2009.

[29] S. Agarwal, A. Aurora and A.Jain, "Catalytic effect of ZrCrNi alloy on hydriding properties of MgH$_2$", J. Hydrogen Energy, Vol. 34, pp. 9157-9162, 2009.

[30] R.A. Varin, T. Czujko, Ch. Chiu, R. Pulz and Z.S. Wronskic, "Synthesis of nanocomposite hydrides for solid-state hydrogen storage by controlled mechanical milling techniques", J. Alloys Compd., Vol. 483, pp. 252-255, 2009.

[31] L.-P. Ma, P. Wang and H.-M. Cheng, "Hydrogen sorption kinetics of MgH$_2$ catalyzed with titanium compounds", J. Hydrogen Energy, Vol. 35, pp. 3046-3050, 2010.

[32] J. Mao, Z. Guo, X. Yu, H. Liu and Z. Wu, "Enhanced hydrogen sorption properties of Ni and Co-catalyzed MgH$_2$", J. Hydrogen Energy, Vol. 35, pp. 4569-4575, 2010.

[33] M.Tian and C. Shang, "Nano-structuredMgH2 catalyzed by TiC nanoparticles for hydrogen storage", Chem. Technol. Biotechnol., Vol. 86, pp. 69-74, 2011.

[34] N. Mahmoudi,A. Kaflou and A. Simchi, "Hydrogen desorption properties of MgH$_2$ –TiCr$_{1.2}$Fe$_{0.6}$ nanocomposite prepared by highenergy mechanical alloying", Power Sources, Vol. 196, pp. 4604-4608, 2011.

[35] G. Liu, Y. Wang, J. Lifang and Y. Huatang, "Solid-state synthesis of amorphous TiB$_2$ nanoparticles on graphene nanosheets with enhanced catalytic dehydrogenation of MgH$_2$", J. Hydrogen Energy, Vol. 39, pp. 38282-3829, 2014.

[36] P. Jain, V. Dixit, A. Jain, O. N. Srivastava and J. Huot "Effect of Magnesium Fluoride on Hydrogenation Properties of Magnesium Hydride", Energies, Vol. 8, pp. 12546–12556, 2015.

[37] A. Kadri, Yi Jia, Z. Chen and X. Yao "Catalitically Enhauced Hydrogen Sorption in Mg-MgH2 by Coupling Vanadium-Based Catalyst and Carbon Nanotubes", Materials, Vol. 8, pp. 3491-3507, 2015.

[38] R.Shahi, P.Tiwari, R.Anand, M.A.Shaz and O.N.Srivastava, "Studies on de/rehydrogenation characteristics of nanocrystalline MgH2 co-catalyzed with Ti, Fe and Ni", J. Hydrogen Energy, Vol. 38, pp. 2778-2784, 2013.

[39] E. Ivanov, I. Konstanchuk, A. Stepanov and V. Boldyrev, "Magnesium mechanical alloys for hydrogen storage", Less-Common Metals, Vol. 131, pp. 25-29, 1987.

[40] H. Imamura, N. Sakasai and Y.Kaji,"Hydrogen absorption of Mg-Based composites prepared by mechanical milling: Factors affecting its characteristics", J. Alloys Compd., Vol. 232,pp. 218-223, 1996.

[41] H. Imamura, N.Sakasai and T.Fujinaga, "Characterization and hydriding properties of Mg-graphite composites prepared by mechanical grinding as new hydrogen storage materials", J. Alloys Compd., Vol. 253-254, pp. 34-37, 1997.

[42] A. Zaluska, L. Zaluski and J.O. Strom-Olsen, „Nanocrystalline magnesium for hydrogen storage", J. Alloys Compd., Vol. 288, pp. 217-225, 1999.

[43] J.- L. Bobet, C. Even, Y. Nakamura, E. Akiba and B. Darriet "Synthesis of Mg & Ti – hydride via reactive mechanical alloying", J. Alloys Compd., Vol. 298, pp. 279-284, 2000.

[44] J.-L. Bobet, E. Akiba and B. Darriet "Influence of 3d-metal addition on MgH2 synthesize Study of Mg-M (M = Co, Ni, Fe) mixture elaborated by reactive mechanical alloying hydrogen sorption properties", J. Hydrogen Energy., Vol. 26, pp. 493-501, 2001.

[45] H.Imamura, S.Tabata and N.Shigetomi "Composites for hydrogen storage by mechanical grinding of graphite carbon and magnesium", J. Alloys Compd., Vol. 330-332, pp. 579-583, 2002.

[46] H.Imamura, M.Kusuhara and S.Minami, "Carbon nanocomposites synthesized by high-energy mechanical milling of graphite and magnesium for hydrogen storage",Acta Materials, Vol. 51, pp. 6407-6414, 2003.

[47] M.Y. Song, "Hydriding kinetics of a mechanically alloyed mixture Mg - 10 wt % Ni", J. Hydrogen Energy., Vol. 28, pp. 403-408, 2003.

[48] D.Chen, L.Chen and S.Liu, "Microstructure and hydrogen storage property of Mg/MWNTs composites",

J. Alloys Compd., Vol. 372, pp. 231-237, 2004.

[49] C.X.Shang and Z.X. Guo, "Effect of carbon on hydrogen desorption and absorption of mechanically milled MgH$_2$", Power Sources., Vol. 129, pp. 73-80, 2004.

[50] S.Dal Toè, S.Lo Russo and A.Maddalena, "Hydrogen desorption from magnesium hydride–graphite nanocomposites produced by ball milling",Mater. Sci. Eng., Vol. B1082, pp. 24-27, 2004.

[51] S. N. Klyamkin, B.P.Tarasov and E.L. Straz, "Ball milling synthesis and properties of hydrogen sorbents in magnesium hydride-graphite system", Alternative Energy and Ecology., Vol.1, pp. 27-29, 2005.

[52] T. Spassov, V. Rangelova and P.Solsona, "Hydriding/dehydriding properties of nanocrystalline $Mg_{87}Ni_3Al_3M_7$ (M=Ti,Mn,Ce,La) alloys prepared by ballmilling",J.Alloys Compd., Vol. 398, pp. 139-144, 2005.

[53] P. Delchev, P. Solsona and B. Drenchev, "Direct hydriding of $Mg_{87}Al_7Ni_3Mn_3$by reactive mechanical milling in Hydrogen atmosphere and influence of particle size on the dehydriding reaction", J. Alloys Compd., Vol. 388, pp. 98-103, 2005.

[54]T. Spassov, V. Petkov andP. Solsona "Hydriding/dehydridingof $Mg_{87}Ni_3Al_3Mm_7$(Mm=La, Ce-rich mischmetal) alloy produced by mechanical milling", J. Alloys Compd., Vol. 403, pp. 363-367, 2005.

[55] S. Doppiu, P. Solsona, T. Spassov, G. Barkhordarian, M. Dorngeim, T. Klassen, S. Surinach and M.D. Baro, "Thermodynamic properties & absorption-desorption kinetics of Mg87Ni10Al3 alloy synthesized by reactive ball milling under H2 atmosphere*", J. Alloys Compd., Vol. 404-406, pp. 27-30,2005.

[56] R.A. Varin, S. Li, Ch. Chiu, L. Guo, O. Morozova, T. Khomenko and Z. Wronski, "Nanocrystalline and non-crystalline hydrides syntesized by controlled reactive mechanical alloying/milling of Mg – X(X=Fe,Co, Mn, B) systems", J. Alloys Compd., Vol. 404-406, pp. 494-498, 2005.

[57] T. Kondo, K. Shindo and Y. Sakurai, "Dependence of hydrogen storagecharacteristics of Mg-$TiFe_{0,92}Mn_{0,08}$ composite on amount of $TiFe_{0,92}Mn_{0,08}$", J.Alloys Compd., Vol. 404-406, pp. 511-514, 2005.

[58] J. Bystrzycki, T. Czujko and R.A. Varin, "Processing by controlled mechanical milling of nanocomposite powders Mg + X (X = Co, Cr, Mo, V, Y, Zr) and their hydrogenation properties", J. Alloys Compd., Vol. 404-406, pp. 507-510, 2005.

[59] Au. Ming, "Hydrogen storage properties of magnesium based nanostructured composite materials", Mater. Sci. Eng., Vol. B 117, pp. 37- 44, 2005.

[60] A.Ye. Yermakov, N.V. Mushnikov, M.A. Uimin, V.S. Gaviko, A.P. Tankeev,A.V. Skripov, A.V. Soloninin and A.I. Buzlukov, „Hydrogen reaction kinetics of Mg-based alloys synthesized by mechanical milling", J. Alloy Compd., Vol. 425, pp. 367-372, 2006.

[61] T.R. Jensen, A. Andreasen and T.Vegge, „Dehydrogenation kinetics of pure and nickel-doped magnesium hydride investigated by in situ time-resolved powder X-ray diffraction", J. Hydrogen Energy*., Vol. 31, pp. 2052- 2062, 2006.

[62] C.Z.Wu, P.Wang and X.Yao, "Effect of carbon/noncarbon addition on hydrogen storage behaviors of magnesium hydride", J. Alloys Compd., Vol. 414, pp. 259-264, 2006.

[63] H.Imamura, I.Kitazawa and Y. Tanabe, "Hydrogen storage in carbon/Mg nanocomposites synthesized by ball milling",j. Hydrogen Energy., Vol. 32, pp. 2408-2411, 2007.

[64] A.D. Rud, A.M.Lakhnik and V.G. Ivanchenko, "Hydrogen storage of the Mg - C composites", J. Hydrogen Energy., Vol. 33, pp.1310-1316, 2008.

[65]V.D. Dobrovolsky, O.G.Ershova, Y.M.Solonin andO.Y. Khyzhun and A.Y. Koval, "Influence of Ti, Mn, Fe, Ni addition upon thermal stability & decomposition temperature of the MgH_2 phase of alloys synthesized by reactive mechanical alloys", J. Alloys Compd., Vol. 464, pp. 212-218, 2008.

[66] O.G. Ershova, V. D. Dobrovolsky and Y. M. Solonin, "About manner and mechanisms of reduction of thermal firmness of Mg, Ti, Y- based mechanical alloys", In: Carbon Nanomaterials in Clean Energy Hydrogen Systems: The NATO Science for Peace and Security Programme; B. Baranowski et al., Eds.; Springer Science + Business Media B.V., 2008, pp. 429 - 436.

[67]O.G. Ershova, V. D. Dobrovolsky and Y. M. Solonin, "Thermal stability and hydrogen sorption properties of the MgH_2 hydride derived by the reactive milling of the Mg +10 % wt. Ti mixture", In: Carbon Nanomaterials in Clean Energy Hydrogen Systems: The NATO Science for Peace and Security Programme; B. Baranowski et al., Eds.; Springer Science + Business Media B.V., 2008, pp. 467 - 472.

[68] C. Milanese, A. Girella, G. Bruni, V. Berbenni, P. Cofrancesco, A. Marini, M. Villa and P. Matteazzi, "Hydrogen storage in magnesium–metal mixtures: Reversibility, kineticaspects and phase analysis", J. Alloys Compd., Vol. 465, pp. 396 – 405, 2008.

[69] K. Sung Nam, Baek Sung Hwan, R. Daniel, S.-H. Hong and M.Y. Song, "Enhancement of the hydrogen storage characteristics of Mg by reactive mechanical grinding with Ni, Fe and Ti", J. Hydrogen Energy., Vol. 33, pp. 4586 – 4592, 2008.

[70] R.V. Denys, A.B. Riabov, J.P. Maehlen, M.V. Lototsky, J.K. Solberg and V.A. Yartys, "In situ synchrotron X-ray diffraction studies of hydrogen desorption and absorption properties of Mg and Mg-Mm-Ni after reactive ball milling in hydrogen", Acta Materials., Vol. 57, pp. 3989 – 4000, 2009.

[71] K.G. Bambhaniya. G.S. Grewal, V. Shrinet, N.L. Sindh andT.P. Govindan, "Hydrogen storage properties of MgH_2 - Sic composites", J. Hydrogen Energy., Vol. 37, pp. 3671-3676, 2012.

[72] V.D. Dobrovolsky, O.G.Ershova and Y.M.Solonin, "Thermal resistance and the kinetics of hydrogen desorption from hydrides of the Mg–Al–Ni–Ti mechanical alloy", Materials Science, Vol. 51, No. 4, 2016; DOI:10.1007/s11003-016-9862-z.

[73] V.D. Dobrovolsky, O.G.Ershova, Y.M.Solonin andA.Y. Koval, "Thermal stability and kinetics of hydrogen desorption from MgH_2 phase of mechanical alloyMg +10 % wt. Al +10 % wt.Ti", Vidnovlyuvana Energetika, Vol. 3, pp. 5 -12, 2015 (Ukraine).

[74]V.D. Dobrovolsky, O.G.Ershova , Y.M.Solonin andO.Y. Khyzhun, "Influence of titanium and iron additives to magnesium upon hydrogen-sorption properties, thermal stability and kinetics of hydrogen desorption from MgH_2 phase of mechanical alloy", Powder Metallurgy & Metal Ceramics, Vol. 55, No. 7, pp. 477-488; DOI: 10.1007/S11106-016-9830-z

[75] V.D. Dobrovolsky, O.G.Ershova , Y.M.Solonin andA.Y. Koval "Influence Al and Fe upon thermal stability and kinetics of hydrogen desorption from MgH_2 phase of mechanical alloy", Physics and Chemistry of solid state, Vol. 16, No3, pp. 576-585, 2015 (Ukraine).

[76] R. Florianoa, D. Leivab, J. G. Dessib, A. Augusto Cesário Assellic, A. M. Jorge Juniorb and W. J. Bottab, "Mg-based Nanocomposites for Hydrogen Storage Containing Ti-Cr-V Alloys as Additives", Materials Research, DOI: 10.1590/1980-5373-MR-2016-0179.

[77]O.G. Ershova, V.D. Dobrovolsky, Y.M.Solonin,O.Y. Khyzhun andA.Y.Koval,"The effect of Al on thermal stability and kinetics of decomposition of MgH_2 prepared by mechanochemical reaction at different conditions", Materials Chemistry and Physics, Vol. 162, pp.408-416, 2015.

[78] M. Bououdina and Z.X. Guo, "Comparative study of mechanical alloying of (Mg1Al) and (Mg1Al1Ni)mixtures for hydrogen storage", J. Alloys Compd., Vol. 336, pp. 222-231, 2002.

[79] M. Tanniru, D.K. Slattery and F. Ebrahimi, "Study of stability of MgH_2 in Mg-8at% Al alloy powder", J. Hydrogen Energy., Vol. 35, pp. 3555-3564,2010.

[80] M. Tanniru, D.K. Slattery and F. Ebrahimi, "A study of phase transformation during the development of pressure – composition - isotherms for electrodeposited Mg-Al alloys", J. Hydrogen Energy., Vol. 36, pp. 639-647, 2011.

[81] C. Zhou, Z.Z. Fang, J. Lu, X. Luo, C. Ren, P. Fan, Y. Ren and X. Zhang,"Thermodynamic Destabilization of Magnesium Hydride Using Mg-Based Solid Solution", Phys.Chem. C., Vol. 118, pp. - 11526-11535, 2014.

[82] S. Bouaricha,L.P. Dodelet, D. Guay, J. Huot, S. Boily and R. Schulz, "Hydriding behavior of Mg–Al and leached Mg–Al compounds preparedby high-energy ball-milling", J. Alloys Compd., Vol. 297, pp. 282-293, 2000.

[83] Z. Li, X. Liu, L. Jiang and S. Wand, "Characterization of 20wt%Ni-Y hydrogen storage

composite prepared by reactive mechanical alloying", J. Hydrogen Energy, Vol. 32, pp. 1869-1864, 2007.

[84] R. Shahi, R.Tiwari, P.Anand, M.A.Shaz and O.N.Srivastava, "Studieson de/rehydrogenation characteristicsof nanocrystalline MgH2 co-catalyzed with Ti,Fe and Ni", J. Hydrogen Energy., Vol. 38, pp. 2778 – 2784, 2013.

[85] Y. Wang, X.-qin Zeng, J.-X. Zou, D.-J. LI, X.-M. Wu and W.-J. Ding, "Microstructure characterization and hydrogen desorption behaviors of Mg−Al−H powders prepared by reactive milling in hydrogen", Trans.Nonferrous Met. Soc. China., Vol. 23, pp. 3112−3118, 2013.

[86] J.F. Stampfer, C.E. Holley and J.F. Suttle, "The Magnesium-Hydrogen System", Am. Chem.Soc., Vol. 82, pp. 3504 – 3508, 1960.

[87] K.G. Bambhaniya, G.S. Grewal, V. Shrinet, N.L. Sindh and T.P. Govindan, "Fast hydriding Mg-Zr-Mn-Ni alloy composition for high capacity hydrogen storage application", J. Hydrogen Energy., Vol. 37, pp. 3671-3676, 2012.

[88] L. Haizhen,X. Wang,Y. Liu,Z. Dong, S. Li, H.Ge, M.Yan, "Microstructures and Hydrogen Desorption Properties of the MgH2−AlH3 Composite with NbF5 Addition", Phys. Chem. C., Vol. 118, pp. 18908−18916, 2014.

[89] H. Liu,X. Wang,Y. Liu,Z. Dong, G. Cao, S. Li, M. Yan, "Improved hydrogen storage properties of MgH2 by ball milling with AlH3 preparations, de/rehydriding properties and reaction mechanisms", Materials Chemistry A., Vol.1, pp. 12527-12535, 2013.

[90] C. Zhou,Z. Zak, R. Fang, J. Li and J. Lu, "Effect of Ti Intermetallic Catalysts on Hydrogen Storage Properties of Magnesium Hydride", Phys.Chem., Vol. 117, No 25, pp. 12973-12980, 2013.

[91] S.F. Santos, T.T. Ishikawa, W.J. Botta and J. Huot, "MgH2 + FeNb nanocomposites for hydrogen storage", Materials Chemistry and Physics,Vol. 147, pp. 557-562, 2014.

[92] H.Yu, S. Bennici and A. Auroux, "Hydrogen storage and release: Kinetic and thermodynamic studies of MgH2 activated by transition metal nanoparticlecs", J. Hydrogen. Energy., Vol. 39, pp. 11633-11641, 2014.

[93] M. Shimada, H. E. Tamaki and H. Inoue, "Kinetic analysis for hydrogen absorption and desorption of MgH2 – based composites", Materials and Chemical Engineering, Vol. 2, no 3, pp. 64 – 71, 2014.

[94] Z. Min, Y. Lu, L. Ouyang and Hui Wangm, "Thermodynamic Tuning of Mg-Based Hydrogen Storage Alloys", Materials, Vol. 6, pp. 4654-4674, 2013.

[95] V.D. Dobrovolsky, O.G. ErshovaO.Y. Khyzhun andY.M. Solonin,"Influence of exposure to air and mechanical dispersion upon thermal stability and decomposition tem-perature of β-MgH2 phase, a component of composites derived by different methods", Current Physical Chemistry., Vol. 4, no1,pp. 106 – 114, 2014.

[96] V.D. Dobrovolsky, O.G. Ershova andY.M. Solonin, "Investigation the impact of obtaining MgH2 and its exposing in the open air on its thermal stability and hydrogen desorption kinetics", Vidnovlyuvana Energetika, No 1, pp.14 -22, 2015 (Ukraine).

[97] C. Zhou, Z.Z. Fang J. Lu and X. Zhang, "Thermodynamic and kinetic destabilization of magnesium hydride using Mg-In solid solution alloys", Am.Chem.Soc., Vol. 135, pp. 10982-10985, 2013.

[98] F.P.Luo, H.Wang, L.Z.Ouyang, M.Q.Zeng, J.W.Liu and M.Zhu,"Enhanced reversible hydrogen storage propertiesof a Mg-In-Y ternary solid solution", J. Hydrogen Energy., Vol. 38, pp. 10912-10916, 2013.

[99] L.Z. Ouyang, Z.J. Cao, H. Wang, J.W. Liu, D.L. Sun, Q.A. Zhang and M. Zhu, "Enhanced dehydriding thermodynamics and kinetics in Mg(In)-MgF2 composite directly synthesized by plasma milling", J. Alloys Compd., Vol. 586, pp. 113-117, 2014.

[100] Z. Cao, L. Ouyang, Y. Wu, H. Wang, J. Liu, F. Fang, D. Sun, Q. Zhang and M. Zhu, "Dual-tuning effects of In, Al, and Ti on the thermodynamics and

kinetics of Mg85In5Al5Ti5 alloy synthesized by plasma milling", J. Alloys Comp., Vol. 623, pp. 354–358, 2015.

[101] B. Delhomme, A. Lanzini, G.A. Ortigoza-Villalba, S. Nachev, P. de Rango, M. Santarelli, P. Marty and P. Leone, "Coupling and thermal integration of a solid oxide fuel cell with a MgH2 tank", J. Hydrogen Energy,Vol. 38, pp. 4740–4747, 2013.

[102] M.V. Lototskyy, I. Tolj, L. Pickering, C. Sita, F. Barbir and V. Yartys, "The use of metal hydrides in fuel cell applications", Progress in Natural Science: Materials International, Vol. 27, No.1, pp 3–20, 2017.