International Science Journal of Engineering & Agriculture
2023; 2(2): 125-141
https://isg-journal.com/isjea/
doi: 10.46299/j.isjea.20230202.12
ISSN: 2720-6319
INTERNATIONAL SCIENCE GROUP

Effect of Ti additive and preparation procedure on the temperature and decomposition kinetics of the MgH_2 phase in the synthesized mechanicals alloys

Olga Ershova
Frantsevych Institute for Problems of Materials Science, National Academy of Sciences of Ukraine
ORCID: 0000-0003-1812-862X

Valentin Dobrovolsky
Frantsevych Institute for Problems of Materials Science, National Academy of Sciences of Ukraine
ORCID: 0000-0002-7325-4103

Yuriy Solonin
Frantsevych Institute for Problems of Materials Science, National Academy of Sciences of Ukraine
ORCID: 0000-0002-8068-1023

To cite this article:
Ershova Olga, Dobrovolsky Valentin, Solonin Yuriy. Effect of Ti additive and preparation procedure on the temperature and decomposition kinetics of the MgH^2 phase in the synthesized mechanicals alloys. International Science Journal of Engineering & Agriculture Vol. 2, No. 2, 2023, pp. 125-141. doi:10.46299/j.isjea.20230202.12.
Received: 03 01, 2023; **Accepted:** 03 06, 2023; **Published:** 04 01, 2023

Abstract: The mechanical alloy Mg + 10 wt.% Ti and two mechanical alloys MgH_2 + 10 wt.% Ti were synthesized by a reactive mechanical alloying (RMA) method, but in different ways. The influence of doping and the preparation procedure of mechanical alloys (MAs) on thehydrogen sorption properties, temperature and decomposition kinetics of their MgH_2 phase was investigated by isobaric thermodesorption spectroscopy at a constant hydrogen pressure of 0.1 MPa. The desorption kinetics of the milled MgH_2 + 10 wt.% Ti are faster than in the case of the ball milled Mg + 10 wt.% Ti. It was found that the manner of obtaining a mechanical alloys by reactive milling of MgH_2 +10 wt. % Ti powder mixture rather than Mg +10 wt. % Ti powder mixture to improve the kinetic characteristics. The role of Ti as an alloying element in improving the hydrogen desorption kinetics of MAs obtained by various preparation procedures was studied. The stabilizing effect of Ti on the nanocrystalline structure and growth of the crystallites (grains) of the MgH_2 phase during the cycling was also evaluated. It has been established the practical absence of the influence of Ti additive and the manner of obtaining MAs on the its thermodynamic stability.

Keywords: mechanical alloy, hydrogen-sorption properties, kinetics, thermal stability, hydride phase.

1. Introduction

Recent research on materials for hydrogen storage has been largely devoted to magnesium hydride MgH_2 and its alloys obtained by mechanochemistry [1-8].The synthesis of magnesium dihydride, MgH_2, with low temperature and high kinetics of its dissociation, high hydrogen capacity and cyclic stability (i.e. with properties that are very important for the practical use of MgH_2) is a problem, despite a significant number of studies aimed at solving it [9, 10].

Most often, the problem of obtaining of MgH2 with several desired characteristics is realized by mechanical dispersion of commercial hydride in the presence of various catalytic additives (e.g., 3d and 4d transition metals [3, 4, 11-18] and their oxides [19-26], fluorides [27-29], intermetallic compounds, nontransition metals such as Al, Cu, Zn, In and Sn, graphite, etc. [30-39]). Many researchers use the different approaches to mill Mg powder with the above mentioned additives in a hydrogen atmosphere (reactive milling) or in an inert atmosphere followed by its direct hydrogenation from the gas phase [1, 5, 9, 10, 40-56].

The majority of researchers are focused on the search for ways to solve the problem of improving the kinetics of magnesium hydrogenation and MgH_2 dehydrogenation [14, 57-64]. Various methods are used to prevent the negative influence of the oxide/hydroxide surface layer on dissociative chemisorption processes and hydrogen recombination, and to reduce the diffusion paths in the solid matrix by minimizing the grain size. Mechanical dispersion processes of commercial MgH_2 or Mg with various catalytic additives under inert or hydrogen atmospheres are widely utilized for this purpose. The influences of the nature of the additive and its structure, as well as the mechanical activation treatment, on the kinetic properties of the MgH_2 hydride phase of mechanical alloys are currently gaining increasing attention [65–77]. The authors [77] report on the effect of Ti-based catalysts (nano-Ti, nano-TiO_2, and $Ti_2Fe_2O_x$ suboxide powders) on hydrogen absorption during reactive milling and desorption in vacuum during further cycling. It was shown that when selecting alloying elements and additives for magnesium, their possible negative effect on the hydrogen capacity of MA, reversibility of the hydrogenation/dehydrogenation process, and stability of the resulting nanostructures [78] should be taken into account. The effect of the preparation procedure, size factor, chemical state of the surface at decreasing temperatures, as well as the improvement of the decomposition kinetics of the MgH_2 phase of mechanical alloys has been shown [79-81].

It should be noted that a noticeable positive effect of the influence of a small addition of5–10 wt. % transition metal (e.g., Ti, Ni, Fe, etc.) on the hydrogen capacity and the rate of the cyclic process of sorption/desorption of hydrogen from MgH_2phase was observed by the researchers during the preparation (synthesis) both by reactive grinding of commercial MgH_2 powder with the addition of TM, and by grinding magnesium metal powder with the same TM additive. At the same time, attention should be paid to the different conditions for obtaining hydrogen sorption characteristics and the kinetic curves of hydrogen desorption from mechanical alloys obtained by different of the above manners. By this we mean the different temperatures and hydrogen pressures at which the kinetic curves of hydrogen desorption of MA were obtained. This fact practically does not allow to make a correct comparison of the experimental data received by various researchers and to define a way and conditions of reception of MAs which are capable to provide the best and stable hydrogen sorption and kinetic characteristics under the cycling conditions.

The purpose of this work was to study the role of the manner and conditions of production, as well as the size factor, in reducing the temperature and improving the decomposition kinetics of the nanosized MgH_2 phase of Mg–Ti mechanical alloys obtained by various manners, but one method - reactive mechanical alloying (RMA).

A probable dependence of the improvement in the hydrogen sorption and kinetic characteristics of MgH_2 phase on the manner of its preparation and the additives nature and structure of the additives was expected. The study of this dependency was also the purpose of this work.

2. Materials and methods

Commercial powders of Mg (Alfa Aesar <100 μm, 99.8% purity metal basis) and Ti (purchased from the Zaporizhzhya Titanium-Magnesium Industrial Plant with a purity of 99.98 % and particle size of 6 μm) were used as raw materials. Three mechanical alloys of magnesium with an addition of 10 wt.% Ti, denoted as MA1, MA2, MA3, were synthesized by reactive mechanical alloying (RMA) in different manners. Mechanical alloy MA1 was obtained by reactive milling of Mg powder with Ti for 20 h, while mechanical alloy MA2 was obtained by reactive milling of MgH_2 powder (obtained by hydrogenation of Mg powder from the gas phase) with Ti additive under the same milling conditions. Mechanical alloy MA3 was prepared by a different process. MgH_2 was obtained by reactive milling of magnesium powder for 10 h, after which 10 wt.% Ti was added and reactive milling was continue dundera hydrogen atmosphere for a further 10 h. The total reactive milling time in the latter case, as in the case of MA1 and MA2, was 20 h. For comparison, MgH_2 powder without Ti addition (sample MA4) was obtained under the same conditions of reactive milling of magnesium powder in a hydrogen atmosphere for 20 h. Mechanical alloying by reactive milling of all powder mixtures was carried out in a Retch PM 100 planetary ball mill with 10 mm steel balls in a hydrogen atmosphere at a pressure of 1.2 MPa and a speed of 450 rpm. The weight ratio of balls to powder was 20:1.Direct hydrogenation from the gas phase (HGP) of MA1–MA4 was performed at a 5.0 MPa hydrogen pressure and 400 ^oC in the reactor after synthesis of the samples.

An automated computerized DRON-3M diffractometer was employed for X-ray phase and structure analysis of the samples. X-ray diffraction patterns were obtained using Cu Kα - radiation with a graphite monochromator. The profiles of the diffraction lines were plotted with a scan step of 0.10 and 20 s exposure at each point of the spectrum. The crystal lattice parameters and the unit cell volume of the MgH_2 phase in the obtained MAs were analyzed using the Full Prof software Powder Cell 2.4 (https://powdercell-for-windows. software. informer. com /2.4/). The size of the crystallites (grains) of the MgH_2 phase in all MAs was determined by the approximation method according to the Selyakov-Scherrer equation $D_{h,k,l} = 0.94\,\lambda / \beta \cos \theta$. The changes in the size of the powder particles during the mechanical milling process were studied using a Super-Probe 733 scanning electron microscope (not shown).

Investigations of the effect of Ti on the thermal stability, kinetics of hydrogen desorption from the MgH_2 phase were performed by thermodesorption spectroscopy (TDS) on acustom-made automatic computerized apparatus of the original design of V.D. Dobrovolsky [5]. The equipment allows to obtain spectra and curves of hydrogen thermodesorption from hydride by the isobaric method, i.e. to measure the volume of desorbed hydrogen from a sample heated at a given rate in a hydrogen medium at its constant reactor pressure of 0.1 MPa.

3. Results and discussion

3.1. X-ray diffraction analysis

X-ray diffraction patterns of samples MA1, MA2, MA3 after their synthesis by the RMA method are shown in fig. 1 and after their direct hydrogenation from the gas phase in fig. 2. Information on the phase composition of the MA samples obtained by RMA and after hydrogenation from the gas phase (HGP) is given in Table 1.

As can be seen from Fig. 1 and Table 1, samples MA1, MA2, MA3 are composed of MgH_2 with a tetragonal structure, TiH_2 and MgO phases. All MAs show no changes in their phase composition after the first hydrogenation/dehydrogenation cycles from the gas phase (fig. 2).

Table 1. Phase composition of MAs after RMA and after the first 5 cycles of HGP

Mechanical alloys	Phase composition	
	RMA	HGP
MA1 (Mg+10wt.% Ti)	$MgH_{2,}$ TiH_2, MgO	MgH_2, TiH_2 MgO
MA2 (MgH_2+10wt.% Ti)	MgH_2, TiH_2, MgO	MgH_2, $TiH_{2,}$ MgO
MA3 (MgH_2+10wt.% Ti)	$MgH_{2,}$ MgO, TiH_2	$MgH_{2,}$ TiH_2 MgO,
MA4 (Mg without Ti)	Mg, $MgH_{2,}$ MgO	Mg, MgH_2, MgO

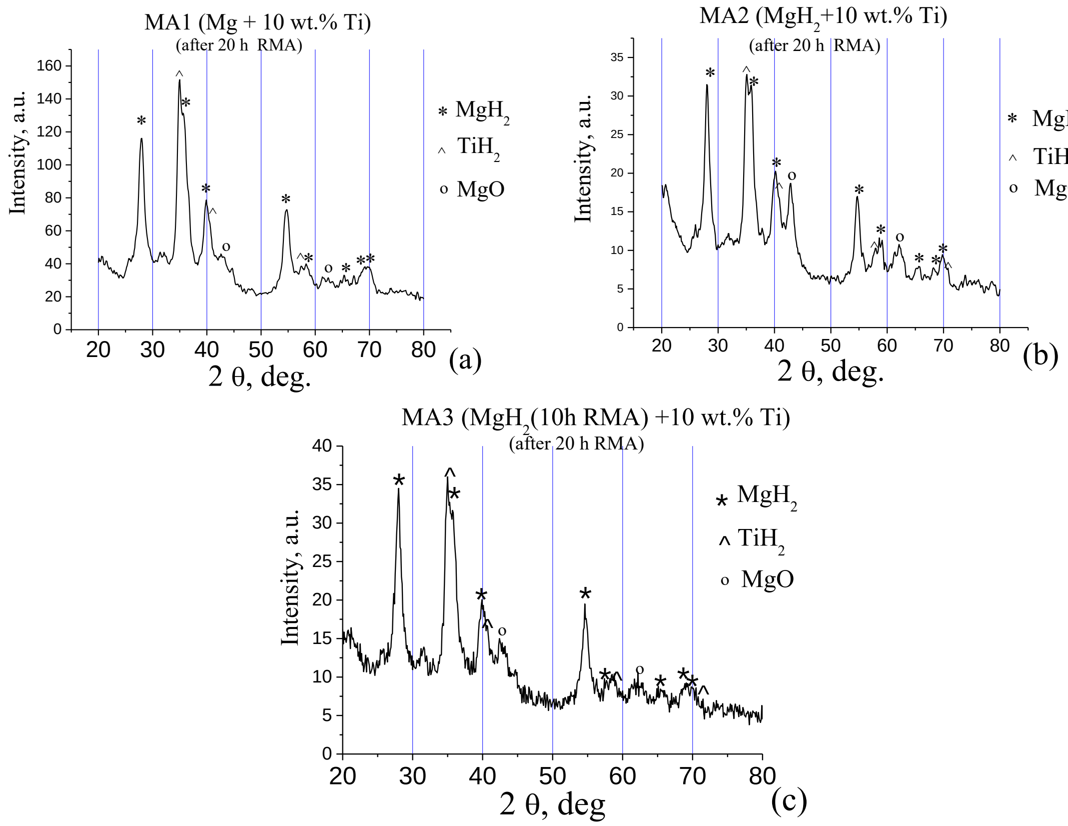

Fig. 1. X-ray diffraction patternsof mechanical alloys after their synthesis by the RMA method: (a) - MA1; (b) - MA2; (c) - MA3.

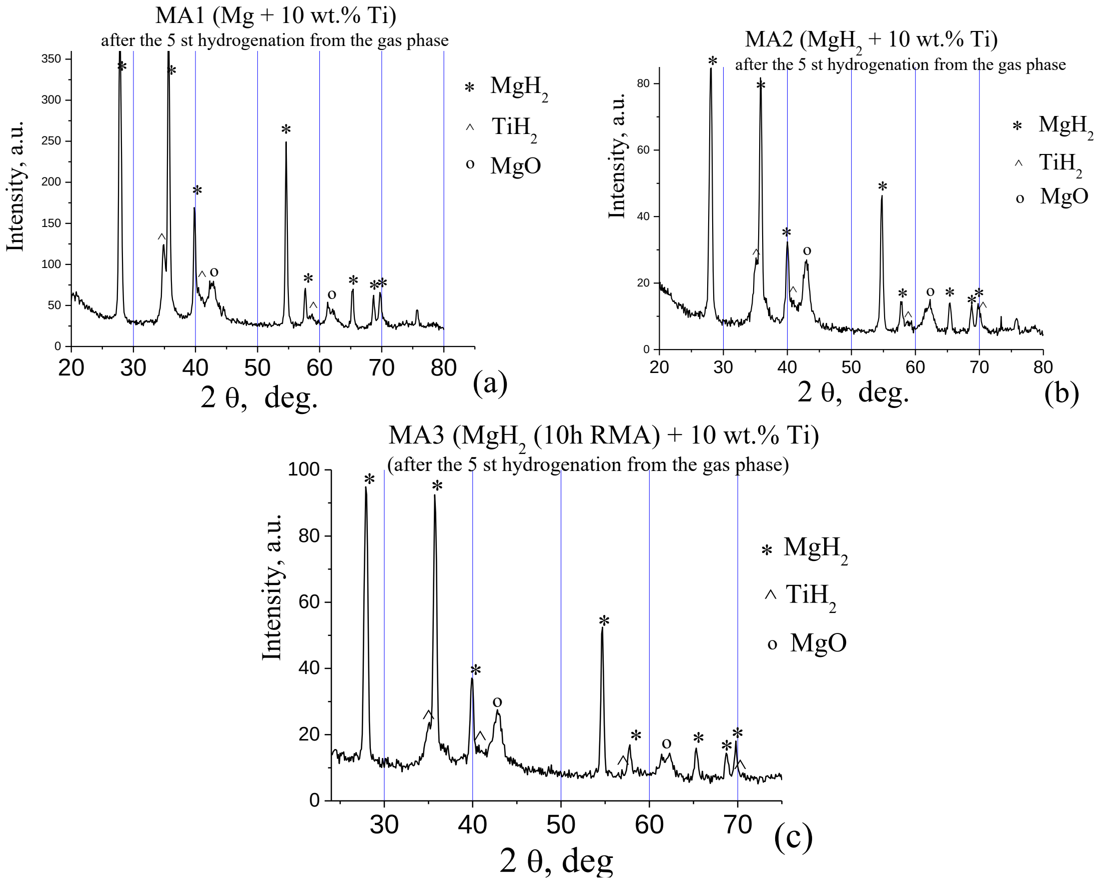

Fig. 2. X-ray diffraction patternsof mechanical alloys after their direct hydrogenation from the gas phase: (a) - MA1; (b) - MA2; (c) - MA3.

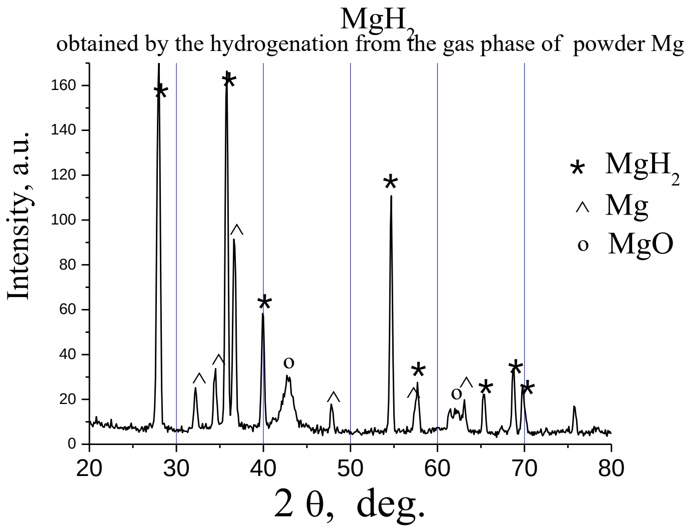

Fig. 3. X-ray diffraction pattern of a non-commercial MgH^2 specimen.

Fig. 3 shows the X-ray diffraction pattern of the non-commercial MgH_2powder used to obtain the MA2 sample. This hydride was obtained by direct hydrogenation from the gas phase of magnesium powder with an average particle size of 100 μm at a temperature of 400 °C and a hydrogen pressure of 5 MPa in the reactor.

The crystal lattice parameters and the unit cell volume for the MgH_2 phase of the MA1-MA4 samples are listed in Table 2. The data on the average particle sizes of MA1, MA2, and MA3 powders, determined on the basis of the experimental data of scanning electron microscopy after their synthesis (RMA), and the data on the crystallite (grain) size of the MgH_2 phase in all MAs are given in Table 3.

Table 2. Crystal lattice parameters and unit cell volume of the MgH^2 phase formed in MAsafter RMA and after the first 5 cycles of HGP.

Mechanical alloys	a,c – Å; V-Å^3	
	after RMA	after HGP
MA1	a = 4.4618 c = 3.0411 V = 60.541	a = 4.5089 c = 3.0175 V = 61.346
MA2	a = 4.5020 c = 3.0200 V = 61.209	a = 4.5154 c = 3.0224 V = 61.623
MA3	a = 4.4971 c = 3.0122 V = 60.918	a = 4.5126 c = 3.0199 V = 61.496
MA4	a = 4.5232 c = 3.0161 V=61.707	a = 4.5140 c = 3.0195 V = 61.526

Table 3. Crystallite size and average particle size of the nanosized MgH_2 phase formed in Mas after 20 h of RMA and after the first 5 cycles of HGP.

Mechanical alloys	Crystallite size, nm		$D_{avg.}$, μm
	after RMA	after HGP	RMA
MA1 (Mg+10wt. % Ti)	8.1	30.5	0.4
MA2 (MgH_2+10wt. % Ti)	11.4	31	0.35
MA3 (MgH_2+10wt. % Ti)	12.6	31.8	0.4
MA4 (Mg without Ti)	12	142	0.69

As can be seen from Table 3, the size of crystallites (grains) of the MgH_2 phase after the first 5 cycles of the hydrogenation from the gas phase was found to be 30.5 nm, 31 nm,31.8 nm, and 142 nm for MA1, MA2, MA3, and MA4, respectively, using the obtained X-ray diffraction patterns and the approximation method according to the Selyakov-Scherrer equation $D_{h,k,l} = 0.94\ \lambda / \beta \cos \Theta$. There is an interesting and important fact to be noted in the analysis of the data presented in Table 3. After 5 cycles of heating/cooling of samples MA1, MA2, MA3 during their HGP, the grain size of the MgH_2 phase increased by 3.76, 2.72, and 2.52 times, respectively. However, under the same conditions of cyclic heating/cooling of the MA4 sample (without Ti), an increase in the grain size of from 12 nm to 142 nm (almost 12 times) can be observed. This observation allows a meaningful conclusion to be drawn about the influence of Ti on the stability of the performance characteristics in the studied Mg-based mechanical alloys with Ti additive. By preventing the growth of MgH_2 crystallites (grains), Ti ensures the stability of the nanostructure during cyclic operation and thus the stability of the operating kinetic and hydrogen sorption characteristics.

3.2. Thermal behavior of mechanical alloys MA1, MA2, MA3

In order to determine the effect of the Ti doping procedure on the thermal stability and decomposition temperature of the obtained MA1-MA4 samples, the hydrogen desorption process was studied by the TDS method at a constant hydrogen pressure of 0.1 MPa in the reactor and a sample heating rate of 3 deg/min. The hydrogen desorption isobars obtained during the first heating after RMA of the MA1-MA4 samples are shown in fig. 4, while those obtained after the first hydrogenation from the gas phase are depicted in fig. 5.

Using the obtained hydrogen desorption isobars shown in fig. 4 and fig. 5, the hydrogen capacity and the onset temperature of hydrogen desorption(T_{onset}) for the MgH_2 phase were determined during heating of theMA1-MA4 samples, both after RMA synthesis and after direct hydrogenation from the gas phase (HGP). The data obtained are presented in Table 4. From analyzing the first hydrogen desorption curves, it was found that as a result of reactive milling for 20 h of magnesium mixtures with the addition of 10 wt.% Ti, hydrogen capacities of 5.6 wt.%, 5.5 wt.%, 5.5 wt.% and 7.4 wt.% can be achieved for samples MA1, MA2, MA3 and MA4, respectively.

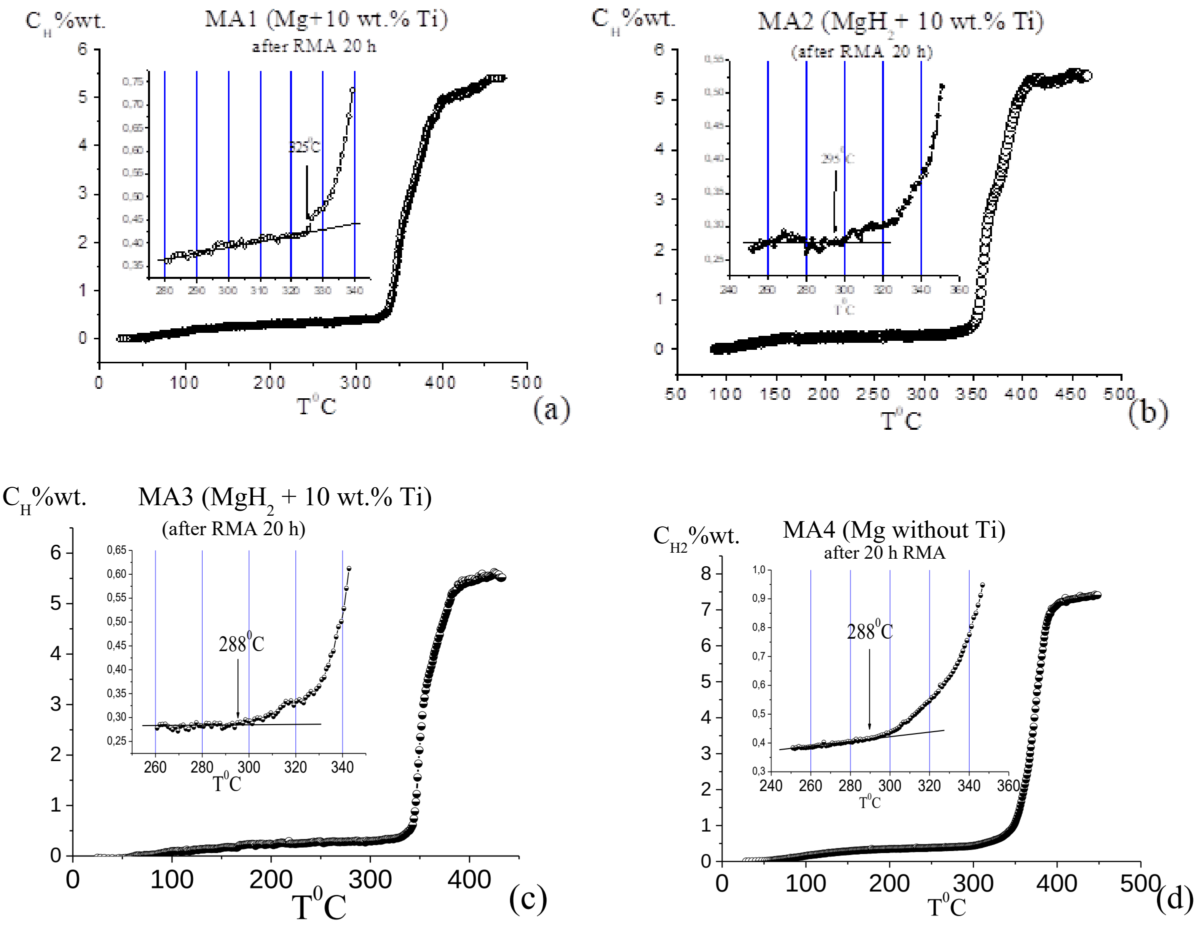

Fig. 4. Hydrogen desorption isobars obtained after synthesis by RMA method of mechanical alloys: (a) - MA1; (b) - MA2; (c) - MA3, (d) - MA4.

Table 4. Onset temperature of hydrogen desorption (T_{onset}) for the MgH_2 phasein MA1-MA4 samples and their hydrogen capacity.

Mechanical alloys	after RMA		after HGP, 1st cycle hydrogenation	
	T_{onset}, °C	C_{H2}, wt.%	$T_{onset.}$, °C	C_{H2}, wt.%
MA1(Mg + 10 wt % Ti)	325	5.6	315	5.3
MA2(MgH_2 +10 wt % Ti)	295	5.5	307	5.1
MA3(MgH_2+ 10 wt % Ti)	288	5.5	310	5.2
MA4(Mg without Ti)	288	7.4	290	6.3

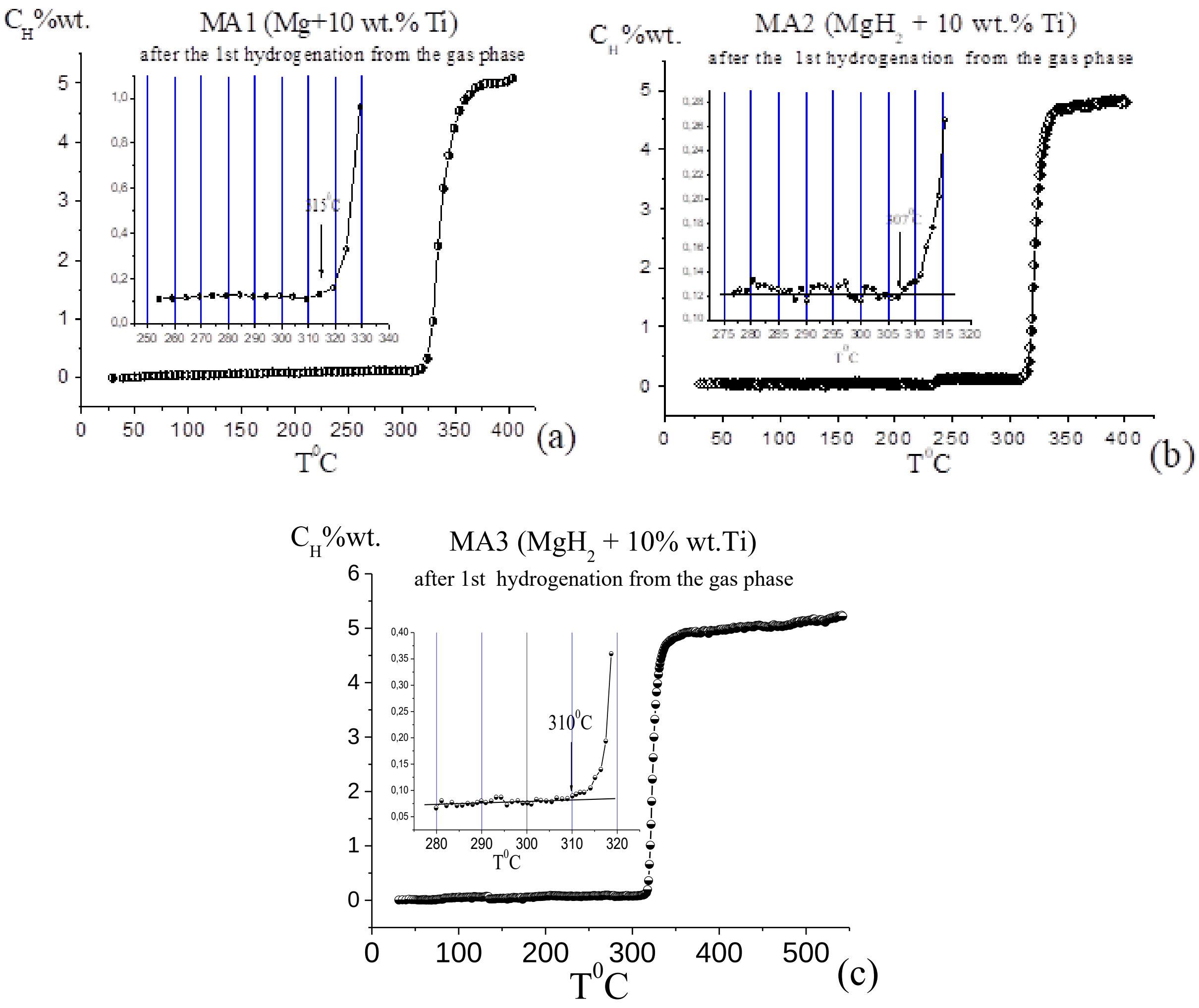

Fig. 5. Hydrogen desorption isobars after the first direct hydrogenation from the gas phase of mechanical alloys: (a) - MA1; (b) - MA2; (c) - MA3.

As can be seen from fig. 4 and fig. 5 and also from the data listed in Table 4, the onset temperature (T_{onset}) was 325°C,295°C, 288°C, and 288 °C for samples MA1, MA2, MA3, and MA4, respectively, after their synthesis by RMA. After the first HGP of these MAs, T_{onset} was determined to be 315°C, 307°C, 310°C, and 290 °C, respectively. It is noteworthy that these temperatures can be considered as the onset temperatures of hydrogen desorption for the main hydride phase (MgH_2), while the onset temperature of TiH_2 cannot be detected due to its low concentration in samples MA1-MA3.When comparing in Table 4 the T_{onset} values for the undoped MA4 sample(288 °C at a hydrogen pressure of 0.1 MPa) with those for MA1-MA3, we can see that there is virtually no effect of the Ti additive and the preparation procedure on the onset temperature, and the associated onset temperature of the MgH_2 phase decomposition can be stated for all MAs. We also did not observe the expected decrease in the equilibrium decomposition temperature of the MgH_2 phase for the above mechanical alloys at a hydrogen pressure of 0.1 MPa (288 °C according to [6]), which would indicate a decrease in the thermodynamic stability of the MgH_2 phase due to its mechanical alloying with Ti. In our opinion, the explanation for the absence of a decrease in the thermodynamic stability of MgH_2 with the addition of Ti may be due to the fact that no solid solution of Ti in magnesium was formed under the conditions used to obtain the MAs. The evidence for this can be seen in the fact that $Mg(Ti)H_2$ hydride was not obtained according to the XRD data (Table 1), while the presence of the TiH_2 phase in the composites MA1-MA3can be attributed to the substantial amount of Ti. As can be seen from Table 2, the decrease in the unit cell volume of the MgH_2 phase is not observed for MA1-MA3with respect to that of theMA4 sample, indicating that no $Mg(Ti)H_2$was formed under the synthesis conditions.

3.3. Hydrogen desorption kinetics from mechanical alloys MA1, MA2, MA3 obtained by different techniques

The hydrogen desorption kinetics from the MgH_2 phase after HGP was studied for all synthesized MAs at temperatures of 310 °C and 330 °C and a constant hydrogen pressure of 0.1 MPa in the reactor. Isobaric-isothermal kinetic curves of hydrogen desorption for the samples MA1 - MA3 at a temperature of 330 °C are shown in fig. 6. Table 5 summarizes the data for the release time of half of the total amount of hydrogen ($\tau_{1/2}$) and the total amount of hydrogen (τ_f) for all MAs. Fig. 7 shows the curve of the hydrogen desorption kinetic from the mechanical alloy MA4 (without the addition of Ti) obtained under the same conditions as the mechanical alloy MA1.

Table 5. Time (min) of release of half ($\tau_{1/2}$) and total amount of hydrogen (τ_f) from mechanical alloys at temperatures of 310 °C, 330 °C and constant hydrogen pressure of 0.1 MPa.

Mechanical alloys	310 °C		330 °C	
	$\tau_{1/2}$	τ_f	$\tau_{1/2}$	τ_f
MA1 (Mg + 10wt. %Ti)	8,5	25	4.7	14
MA2 (MgH_2 +10 wt. % Ti)	5,2	14	3.1	13
MA3 (MgH_2 + 10 wt. % Ti)	-	-	2.9	9
MA4 (Mg without Ti)	55	160	30	80

The analysis of the experimental data presented in Table 5 allows to conclude that the addition of 10 wt.% Ti to magnesium during the synthesizing of theMA1, MA2, MA3 samples significantly improves the hydrogen desorption kinetics from the nanosized MgH_2 phase of these alloys. This is evidenced by the experimentally recorded 6-fold, 6-fold and 9-fold reduction of the total desorbed hydrogen release time for MA1, MA2 and MA3, respectively, at a constant temperature of 330 °C and a constant pressure of 0.1 MPa compared to the time of release of the total amount of hydrogen in the case of MA4. A similar effect of improving hydrogen desorption kinetics by the addition of Ti to Mg and to MgH_2 was observed in studies [40,41,43,73,77,82-85] and [3,4,68,70,86-88], respectively. The analysis and comparison of the data presented in Table 5 for the samples MA1 and MA2 allows us to state that a method of reactive milling of the MgH_2 +10 wt.% Ti powder mixture (rather than milling a powder mixture of Mg +10 wt.% Ti) gives the best kinetic characteristics among the synthesized mechanical alloys. As shown in Table 5, the time required to release half of the total hydrogen ($\tau_{1/2}$) from the sample MA1 (Mg + 10 wt.% Ti) and its total amount (τ_f) at the temperature of 330 °C is 4.7 min and 14 min, respectively. For the sample MA2 (MgH_2 + 10 wt.% Ti), these values are 3.1 min and 13 min, respectively.

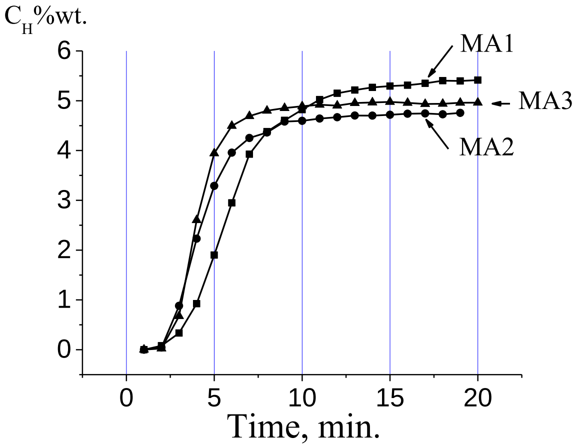

Fig. 6. Kinetic curves of hydrogen desorption of mechanical alloys MA1, MA2, MA3 obtained at the temperature of 330 °C and a constant hydrogen pressure of 0.1 MPa in the reactor.

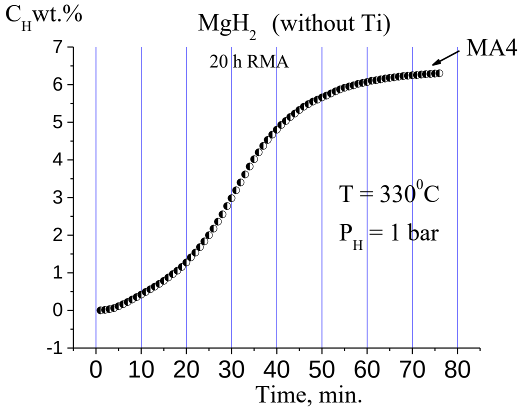

Fig. 7. Kinetic curve of hydrogen desorption of mechanical alloy MA4 obtained at the temperature of 330 °C and a constant hydrogen pressure of 0.1 MPa in the reactor.

To explain this result, the size of the crystallites (grains) of the MgH_2 phase was calculated to be 31 nm and 30.5 nm for MA2 and MA1, respectively, using the obtained X-ray diffraction patterns and the approximation method according to the Selyakov-Scherrer equation $D_{h,k,l} = 0.94\ \lambda /\beta \cos \Theta$ after the first 5 cycles of HGP (Table 3). On the basis of these data, which indicate that the crystallites of the samples MA2 and MA1 are almost identical in size, it is logical to assume that the faster kinetics of hydrogen desorption from the MgH_2 phase in MA2 (MgH_2 + 10 wt.% Ti) is not due to the smaller grain size (and correspondingly shorter diffusion paths for hydrogen atoms) compared to the grain size of the MgH_2 phase in MA1 (Mg + 10 wt.% Ti). As can be seen from Table 3, the crystallite (grain) size of the MA3 sample is 31.8 nm and differs little from those of MA1 and MA2. Thus, according to the data in Tables 3 and 5 (with respect to the size of the crystallites (grains)d (nm) and the time of release of the total amount of hydrogen τ_f (min) in MA1, MA2, MA3), it can be said that there is no correlation between the release time of the total amount of hydrogen from these MAs and their crystallite (grain) size, which depends on the synthesis procedure.

The superior hydrogen desorption kinetics of MA2 compared to MA1 is also not related to the different chemical state of the surface of these mechanical alloys. As we have previously reported [46, 80],the addition of 10 wt.% Ti to magnesium does not change the charge state of the magnesium atoms on the surface of the mechanical alloy because the values of the XPS Mg 2p and Mg 2s core-level binding energies do not change within the accuracy of the measurement when proceeding from the MA sample (without the addition of titanium) to the MA with10 wt.% Ti sample. Moreover, the smaller size of the titanium particles and the greater quantity of ultrafine titanium particles covering each magnesium particle, the better performance of this transition metal as a dispergator, which prevents agglomeration of magnesium particles and allows to obtain a disperse powder of mechanical alloy more rapidly. In our case, titanium becomes very brittle in the early stages of reactive milling due to the formation of titanium hydride and rapidly reduces its particle size. In the next process of cyclic hydrogenation/dehydrogenation, titanium hydride plays the role of a catalyst that significantly accelerates the reaction of magnesium hydrogenation and magnesium hydride dehydrogenation and can act as a "hydrogen pump" [1].

The analysis of the hydrogen desorption kinetic curves shown in Fig. 6, which belong to MA1 and MA2 and have a sigmoid character, allows us to notice their difference. Thus, a longer induction period (up to 3 minutes) of magnesium seed formation due to diffusion can be observed at the beginning of the MA1 curve than at the beginning of the MA2 curve. It can also be seen that the linear part of the MA1 curve from the value of C_H = 1 wt.% to the value of C_H = 4 wt.% has a greater slope than the slope of the corresponding part of the MA2 curve, and thus a lower average rate $\Delta C_H/\Delta t$ of hydrogen desorption from the MgH_2 phase of MA1 than from the MgH_2phase of MA2. Assuming that for both mechanical alloys MA1 and MA2 the formula $dC_H/dt = kC^n$ is valid, where k is the rate constant, the following conclusion can be made. The experimentally observed higher slope of the linear part of the kinetic curve MA1 corresponds to a lower hydrogen desorption rate and a lower rate constant and consequently, a higher activation energy of hydrogen desorption from the MgH_2 phase for the mechanical alloy MA1 than for the alloy MA2.

Thus, the results of our experimental investigations allow us to speak about the different influence of the manner of obtaining on the hydrogen desorption kinetics of the nanosized MgH_2 phase of the mechanical alloys MA1 and MA2. This difference can be seen immediately in the kinetic curves MA1 and MA2 of the hydrogen desorption rate $V = \Delta C_H/\Delta t$ at times $t = \tau_{1/2}$, as shown in Fig. 6. Thus, the value of the hydrogen desorption rate in the case of MA1 was V = 0.95 wt.% / min, and in the case of MA2 it was V = 1.38 wt.% / min, i.e. 1.45 times higher than in the case of MA1. Note that the same conditions were used to perform the experiment and record the kinetic curves MA1 and MA2 (constant temperature (330 °C) and constant hydrogen pressure (0.1 MPa).

A reasonable explanation for the different kinetics of the cyclic hydrogenation / dehydrogenation process of the mechanical alloys Mg + 10 wt.% Ti and MgH_2 + 10 wt.% Ti, in our opinion, can be made by taking into account the influence of the manner of obtaining of these MAs not only on the structure and properties of the main MgH_2 phase, but also on the structure and properties (and their possible change during cycling) of the catalytically active TiH_2 phase formed as a result of RBM.

In our previous publications [89, 90], we reported the effect of a 20 min mechanical treatment in a high-energy mill on the thermal firmness and thermodynamic stability of TiH_2 powder studied by the TDS method at the temperatures of the onset of hydrogen desorption and γ-β phase transformation. After the indicated mechanical treatment of the TiH_2 powder produced in the factory, the release of hydrogen from it during the heating process started already at the temperature of 150–200 °C, in contrast to the temperature of 420–450 °C during the heating of the initial TiH_2 sample. The isobaric hydrogen desorption curve of TiH_2 processed in a planetary ball mill was found to be shifted to lower temperatures by more than 100 degrees compared to the curve of the initial hydride [89].

Therefore, we assume that the TiH_2 phase formed during the synthesis of MA2 may differ from that formed in the MA1 alloy due to different preparation procedures that affect the structural state, grain size, chemical surface state of the particles and, most importantly, the catalytic activity. In turn, the high catalytic activity of titanium hydride, which plays the role of a catalytically active center in the cyclic process of decomposition of the MgH_2phase in the MA2 mechanical alloy, can provide a high rate of recombination of atomic hydrogen and its transport from the MgH_2 lattice to the gas phase and, consequently, the nucleation process and growth of the metallic magnesium phase.

4. Conclusions

Three mechanical alloys of magnesium with an addition of 10 wt.% Ti, denoted as MA1, MA2, MA3, were synthesized by one method of reactive mechanical alloying (RMA), however in different manners. The MA1 alloy was obtained by RMA of Mg powder with Ti for 20 h, while MA2 was prepared by RMA of MgH^2+ 10 wt.% Ti powder (MgH^2 was obtained by hydrogenation of Mg powder from the gas phase) under the same milling conditions. In turn, MA3 was obtained by RMA of Mg powder for 10 h to synthesize MgH^2, then 10 wt.% Ti was added and reactive milling was continued in a hydrogen atmosphere for another 10 h.

The hydrogen capacity, thermal stability, and hydrogen desorption kinetics of the MgH_2 phase in the obtained MAs were investigated by thermodesorption spectroscopy at a constant hydrogen pressure of 0.1MPa.

The time required for desorption of half and total amount of hydrogen from MA1, MA2, MA3 at a constant hydrogen pressure of 0.1MPa and temperature of 330 °C was determined. The manner of obtaining a mechanical alloys by reactive grinding of MgH_2 +10 wt. % Ti powder mixture rather than Mg +10 wt. % Ti powder mixture has been shown to improve the kinetic characteristics.

The role of Ti as an alloying element in improving the hydrogen desorption kinetics of MAs obtained by different manners was studied. The stabilizing effect of Ti on the nanocrystalline structure and growth of the crystallites (grains) of the MgH_2 phase during the cycling was also evaluated. It was found that the thermodynamic stability of the obtained MAs is not affected by the Ti additive and the preparation procedure.

References:

1) Ivanov E.Yu., Konstanchuk I.G., Stepanov A.A. Mechanical alloys magnesium –new materials for hydrogen energy. Report of the Academy of Sciences. 1987. Vol. 286. Nos. 2. P. 385-388.

2) Chen Y., Williams J.S. Formation of metal hydrides by mechanical alloying J. Alloys Comp. 1995. No. 217. P. 181-184.

3) Liang G., Huot J., BoilyS. 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*. 1999. Vol.292 . P. 247-252.

4) Huot J., Liang G., Schulz R. Mechanically alloyed metal hydride systems, Structure of nanocomposite metal hydrides. *Appl. Phys. A* .2001. 72 .P. 187-195; doi: 10.1016/S0925-8388(02)00839-3.

5) Ershova O.G., Dobrovolsky V.D., Solonin Yu.M., Khyzhun O.Yu., Koval A.Y. 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*. 2008. Vol. 464. P. 212-218; DOI: 10.1016/j.jall-com.2007.10.064.

6) Stampfer J.F., Holley C.E., Suttle J.F.The Magnesium-Hydrogen System. *J. Am. Chem. Soc*. 1960. Vol. 82. P. 3504 – 3507;doi: 10.1021/ja01499a006.

7) Pitt M.P., Paskevicius M., Webb C.J., Sheppard D.A., Buckley C.E., Mac A., Gray E. The synthesis of nanoscopic Ti-based alloys and their effectson the MgH2 system compared with the MgH_2 + 0.01Nb2O5benchmark. *Int. J. of Hydrogen energy*. 2012. Vol. 37. P. 4227-4237; doi:10.1016/j.ijhydene .2011.11.114.

8) Sesha Srinivasan, Dervis Emre Demirocak, Ajeet Kaushik, Meenu Sharma,Ganga Ram Chaudhary, Nicoleta Hickman and Elias Stefanakos. Reversible Hydrogen Storage Using Nanocomposites. *Appl. Sci*. 2020. Vol.10. P. 4618- 4629; doi:10.3390/app10134618.

9) Ershova O.G., Dobrovolsky V.D., Solonin Yu. M., Khyzhun O.Yu, Koval A.Yu. 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*. – 2015. – 162. – p.408 – 416.

10) Dobrovolsky V.D., Ershova O.G., Solonin Yu.M., Khyzhun O.Y. 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.* 2016. Vol. 55, Nos. 7.P. 477-488; DOI: 10.1007/S11106-016-9830-z.

11) Huot J., Pelletier J.F., Lurio L.B., Sutton M., Schulz R. Investigation of degydrogenation mechanism of MgH_2–Nb nanocomposites. *J. Alloys Compd*. 2003.Vol. 348. P. 319-324.

12) Shang C.X., Bououdina M., Song Y. Guo Z.X. Mechanical alloying and electronic simulation of (MgH_2 + M) system (M= Al, Ti, Fe, Ni, Cu and Nb) for hydrogen storage. *J. Hydrogen Energy*. 2004.Vol. 29, P. 73-80,

13) Bassetti A., Bonetti E., Pasquini L., Montone A., Grbovic J., Antisari V. Hydrogen desorption from ball milled MgH_2 catalysed with Fe. *Eur. Phys.B* .2005.Vol. 43 P. 19-27.

14) Xie L., Liu Y.and Zhang X. Catalytic effect of Ni nanoparticles on the desorption kinetics of MgH_2 nanoparticles. *J. Alloys Compd*., 2009. Vol. 482, pp. 388-392.

15) Attuluri R., Ba Vijay, Nagaraju D. A Mini Review: Magnesium Hydrides for Hydrogen Storage. *Int. Journal of ChemTech Research.* 2016.Vol.6. Nos. 7. P. 3451-3455.

16) Sun Ze, Lu Xiong, Michael Nyahuma Farai, Yan Nianhua, Xiao Jiankun, Su Shichuan, Liuting Zhang. Enhancing Hydrogen Storage Properties of MgH_2 by Transition Metals and Carbon Materials: A Brief Review. *J. Frontiers in Chemistry*. 2020. Vol. 8. P. 552-566.

17) Chengshang Zhou, Jingxi Zhang, Robert C. Bowman, Jr. and Zhigang Zak Fang. Roles of Ti-Based Catalysts on Magnesium Hydride and Its Hydrogen Storage Properties. *Inorganics chemistry*. 2021. Vol. 9. - 36. P. 9050036- 42; doi.org/10.3390/inorganics9050036.

18) Zahra Akbarzadeh Fatemeh, Rajabi Mohammad. Mechanical alloying fabrication of nickel/cerium/MgH_2 nanocomposite for hydrogen storage: Molecular dynamics study and experimental verification. *J. Alloys Comp.*. 2022. Vol. 899. P. 163280-163291;doi.org/10.1016/j.jallcom.2021.163280.

19) Hanada N., Ichikawa T., Fujii H. Catalytic effect of Ni nano-particle and Nb oxide on H-desorptionproperties in MgH_2 prepared by ball milling. *J.Alloys Compd*. 2005.Nos 404-406.P. 716-719.

20) Borgschulte A., Rector J.H., Dam B. The role of niobium oxide as a surface catalyst for hydrogen absorption. *Catalysis* 2005.Vol. 235.P. 353-358.

21) Hugg P.-A, Dornheim M.,Klassen T. Thermal stability of nanocrystalline magnesium for hydrogen storage. *J. Alloys Compd*. 2005.Nos. 404-406. P. 499-502.

22) Aguey-ZinsouK.-F., Ares- Fernandes J.R., KlassenT. Using MgO to improve the (de)hydriding properties of magnesium. *Mater. Res. Bull*. 2006. Vol. 412. P. 1118-1126.

23) Varin R.A., CzujkoT., Wasmund E.B., WronskiZ.S. Hydrogen desorption properties of MgH_2 nanocomposites with nano-oxides and inco micrometric and nanometric – NiT.*J. Alloys Compd*.2007.Vol. 446-447.P. 63-65.

24) Polanski M., Bystrzycki J. Comparative studies of the influence of different nano-sized metal oxides on the hydrogen sorption properties of magnesium hydride. *J. Alloys Compd*.2009. Vol. 486. P. 697-701.

25) PatahA., Takasaki A. Szmyd J.S.Influence of multiple oxide (Cr_2O_3/Nb_2O_5) addition on the sorption kinetics of MgH_2.*J. Hydrogen Energy*. 2009 Vol. 34, P. 3032-3037.

26) Kosuke Kajiwara, Hisashi Sugime, Suguru Noda, NobukoHanada. Fast and stable hydrogen storage in the porous composite of MgH_2 with Nb2O5 catalyst and carbon nanotube. *J. Alloys Compd*.2022. Vol. 893. P. 162206. doi.org/10.1016/j.jallcom.2021.162206.

27) Ma L.P., KangX.D., DaiH.B., Liang Y., Fang Z.Z.,Wang P.J., Wang P., Cheng H.M. 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*. 2009.Vol. 57, P. 2250-2258.

28) DeleddaS., Borissova A.and. PoinsignononC. H-sorption in MgH_2 nanocomposites containing Fe or Ni with fluorine.*J. Alloys Compd*. 2005.Vol. 404-406. P. 409-412,

29) 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*.2007. Vol. 55. P. 4585-4591.

30) S. Agarwal, A. Aurora and A.Jain. Catalytic effect of ZrCrNi alloy on hydriding properties of MgH_2. *J. Hydrogen Energy*. 2009. Vol. 34, pp. 9157-9162.

31) Ma L.P., Wang P., Cheng H.-M. Hydrogen sorption kinetics of MgH_2 catalyzed with titanium compounds. *J. Hydrogen Energy*. 2010. Vol. 35, pp. 3046-3050.

32) MahmoudiN.,Kaflou A., SimchiA. Hydrogen desorption properties of MgH_2 –$TiCr_{1.2}Fe_{0.6}$ nanocomposite prepared by highenergy mechanical alloying.*Power Sources*. 2011. Vol. 196.P. 4604-4608.

33) HaghparastaM. R., RajabiaM. Hydrogen Desorption Properties of MgH_2- 5at% Ti-Cr-Mn-Fe-V Composite via Combined Vacuum Arc Remelting and Mechanical Alloying.*Procedia Materials ScienceScience Direct 5th International Biennial Conference on Ultrafine Grained and Nanostructured Materials*, UFGNSM15. 2015.P. 605–610. Published by Elsevier Ltd.doi:10.1016/j.mspro.2015.11.091.

34) LiP.C., ZhangJ.W.,HuJ.T., HuangG.,XieL., XiaoH.Y., ZhouX.S., XiaY.H., ZhangJ.C.,ShenH.H. Effects of deuterium content on the thermal stability and deuterium site occupancy of TiZrHfMoNb deuterides. *J. of Solid State Chemistry*. 2021. Vol. 297. P. 121999.

35) Chengshang Zhou, Zhigang Zak Fang, Jun Lu, Xiangyi Luo, Chai Ren, Peng Fan, Yang Ren,and Xiaoyi Zhang. Thermodynamic Destabilization of Magnesium Hydride Using Mg-Based Solid Solution Alloys.*J. Phys. Chem. C* . 2014. 118.P. 11526−11535. dx.doi.org/10.1021/jp501306w.

36) Liu R, Zhao Y, Chu T. Theoretical exploration of MgH_2 andgraphene nano-flakes in cyclohexane: proposing a newperspective toward functional hydrogen storage material.*Chem Commun*. 2015.Vol. Nos. 51.24 P. 29-32.

37) Xia G, Tan Y, Chen X, Sun D, Guo Z, Liu H, et al.Monodisperse magnesium hydride nanoparticles uniformlyself-assembled on graphene. *Adv Mater*. 2015. 27:5981e8.

38) Liu G, Wang Y, Jiao L, Yuan H. Understanding the role of fewlayergraphene nanosheets inenhancing the hydrogensorption kinetics of magnesium hydride. *ACS Appl MaterInterfaces*.2014. No 6. P. 11038-11046.

39) Liu G, Wang Y, Jiao L, Yuan H. Solid-state synthesis ofamorphous TiB2 nanoparticles on graphene nanosheets withenhanced catalytic dehydrogenation of MgH_2. *Int J. HydrogenEnergy*. 2014. No 39. P. 3822 - 3829.

40) Ivanov E., Konstanchuk I., Stepanov A., Boldyrev V. Magnesium mechanical alloys for hydrogen storage. *J. Less-Comm. Metals*. 1987. Vol. 131. P. 25 – 29.

41) BobetJ.- L., EvenC., NakamuraY., AkibaE., DarrietB.Synthesis of Mg & Ti – hydride via reactive mechanical alloying.*J. Alloys Compd*. 2000.Vol. 298.P. 279-284.

42) M.Y. Song. Effectofvtchanicalalloying onthehydrogenstorage characteristicsof Mg-xwt % Ni (x = 0, 5, 10, 25 and 55) mixtures. Int. J. Hydrogen Energy. 1995. Vol. 20, Nos. 3. P. 221 - 226.

43) BobetJ.-L., Akiba E., Darriet B. Influence of 3d-metal addition on MgH_2 synthesizeStudy of Mg-M (M=Co, Ni, Fe) mixture elaborated by reactive mechanical alloying hydrogen sorption properties.*J. Hydrogen Energy*. 2001. Vol. 26, pp. 493-501.

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

45) ErshovaO.G., Dobrovolsky V.D.,SoloninYu. M. About manner and mechanisms of reduction of thermal firmness of Mg, Ti, Y-based mechanical alloys.*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. P. 429 - 436.

46) ErshovaO.G., Dobrovolsky V. D.,SoloninYu. M.Thermal stability and hydrogen sorption properties of the MgH_2 hydride derived by the reactive milling of the Mg +10 % wt. Ti mixture. *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. P. 467 - 472.

47) Lei Z, Liu Z., Chen Y. Cyclic hydrogan properties of Mg milled with nikel nano-powders and NiO. *J. Alloya Comp*.2009. Vol.470, Nos. P. 470 – 472; doi.org/10.10.16/i.jallcom.

48) MilaneseC., GirellaA., BruniG., BerbenniV., CofrancescoP., MariniA., Villa M.,MatteazziP. Hydrogen storage in magnesium–metal mixtures: Reversibility, kinetic aspects and phase analysis. *J. Alloys Compd*. 2008. Vol. 465, pp. 396 – 405, 2008.doi;10.1016/i.jallcom.2007.10.091.

49) Sung NamK., HwanBaek Sung, DanielR., Hong S.-H., SongM.Y.Enhancement of the hydrogen storage characteristics of Mg by reactive mechanical grinding with Ni, Fe and Ti.*J. Hydrogen Energy*. 2008. Vol. 33.P. 4586 – 4592. doi;10.1016/j.ijhydene.2008.05.097.

50) Song Y., Guo Z.X., Yang R. Influence of titanium on the hydrogen storage characteristics of magnesium hydride;first principles investigation. *Materials science & Engineering A.* 2004. Vol. 365. P. 73 – 79. doi:10.1016/j.msea.2003.09.008.

51) Yermakov A.Ye., Mushnikov N.V., Uimin M.A., GavikoV.S., Tankeev A.P., Skripov A.V., Soloninin A.V., Buzlukov A.I. Hydrogen reaction kinetics of Mg-based allys synthesized by mechanical milling. *J. Alloy Compd*. 2006. Vol. 425. P. 367-372. doi:10.1016/i.jallcom.2006.01.039.

52) Baum L., Meyer M., Mendoza-Zelis L. Hydrogen storage properties of the Mg/Fe system. *Physica B*. 2007. Vol. 389. P, 189-192. Doi:10/1016.j.physb.2006.07.054.

53) Won Haa, Ho-Shin Leeb, Jeong-IlYouna, Tae-Whan Hongc,Young-Jig Kim. Hydrogenation and degradation of Mg–10 wt% Ni alloy aftercyclic hydriding–dehydriding. *Int. J. of Hydrogen Energy*. 2007. Vol. 32. P. 1885 – 1889. doi:10.1016/j.ijhydene.2006.08.029.

54) Hye Ryoung PARK, Sung Nam Kwon, Myoung Youp Song. Effects of Milling Time on the Hydrogen Storage Properties of Mg-based Transition Metals-added Alloys. *MATERIALS SCIENCE (MEDŽIAGOTYRA).* 2018. Vol. 24, No. 2. doi.org/10.5755/j01.ms.24.2.18395.

55) Ze Sun, Xiong Lu,Farai Michael Nyahuma, Nianhua Yan, Jiankun Xiao, Shichuan Su and Liuting Zhang. Enhancing Hydrogen Storage Properties of MgH_2 by Transition Metals and Carbon Materials: A Brief Review. Frontiers in Chemistry . 2020. - V. 8. P. 552 – 566.

56) Mohamed Sherif El-Eskandarany. Recent developments in the fabrication,characterization and implementation of MgH_2-based solid-hydrogen materials in the Kuwait Institute for Scientific Research. *RSC Adv*. 2019. 9, 9907–9930;DOI: 10.1039/c9ra00287a.

57) ZhuM., GaoY., CheX.Z., YangY.Q., Chung C.Y. Hydriding kinetics of nano-phase composite hydrogen storage alloys prepared by mechanical alloying of Mg and $MmNi_{5-x}(CoAlMn)_x$ *J. Alloys Compd*. 2002. Vol. 330-332. P. 708-713.http://refhub.elsevier.com/S0925-8388(15)31346-3/sref83.

58) DuA.J., Sean C. Smith,X.D.Yao, Lu G.Q. The Role of Ti as Catalyst for the Dissociation ofHydrogen on a Mg(0001) Surface. *J. Phys. Chem. B.*2005. V. 109. P. 18037-1804; doi:10.1021/jp052804c

59) YuH., Bennici S.and AurouxA. Hydrogen storage and release: Kinetic and thermodynamic studies of MgH_2 activated by transition metal nanoparticlecs.*J. Hydrogen. Energy*. 2014.Vol. 39. P. 11633-11641.

60) M. Shimada, H. E. Tamaki and H. Inoue. Kinetic analysis for hydrogen absorption and desorption of MgH_2 – based composites.*Materials and Chemical Engineering.* 2014.Vol. 2, Nos. 3. P. 64 – 71.

61) N. Patelli, A. Migliori, V. Morandi, L.Pasquini. Interfacesinbiphasicnanoparticlesgive a boostto Magnesium-based hydrogenstorage. httpsdoiorg101016jnanoen2020104654.

62) H. Wang, H.J. Lin, W.T. Cai , L.Z. Ouyang, Zhu M.Tuning kinetics and thermodynamics of hydrogen storage in lightmetal element based systems. A review of recent progress. J. Alloys Comp. 2016. Vol. 658. P. 280 - 300; http://dx.doi.org/10.1016/j.jallcom.2015.10.090.

63) Qun Luo, Jianding Li, Bo Li, Bin Liu, Huaiyu Shao, Qian Li. Kinetics in Mg-based hydrogen materials storage: Enhancement and mechanism. *J.of Magnesium and Alloys.* 2019. Vol. 7. P. 58-71. doi.org/10.10 16/j.jma.2018.12.001.

64) Li Chen, Changyi Hua, Feng Liub. Microstructure and hydrogen storage kinetics ofMg89RE11 (RE - Pr, Nd, Sm) binary alloys. *RSC Adv*. 2019. Vol. 9. P. 4445–4452;doi: 10.1039/c8ra08983c.

65) Pozzo M., Alfè D. Hydrogen dissociation and diffusion on M(=Ti,Zr,V,Fe,Ru,Co,Rh,Ni,Pd,Cu,Ag)-doped Mg(0001). Surfaces. *J. Chem. Phys*. 2008. Vol.128. P. 094703 - http://arxiv.org/abs/0811.2342v1

66) BérubéV., RadtkeG., DresselhausM., ChenG. Size effects on the hydrogen storage properties of nanostructured metal hydrides: A review.*Int. J. Energy Res*. 2007. Vol. 31.P. 637–663; doi:10.1002/er.1284.

67) Asano K., Westerwaal R.J., Anastasopol A., Mooij L.P.A., Boelsma C., Ngene P., Schreuders H., EijtS.W.H., Dam B. Destabilization of Mg Hydride by Self-Organized Nanoclusters in the Immiscible Mg-Ti System. *J. Phys. Chem. C*. 2015. Vol.119. P. 12157–12164; doi:10.1021/acs.jpcc.5b02275.

68) Ying Wang, Qiuyu Zhang, YijingWang, Lifang Jiao, HuatangYuan. Catalytic effects of different Ti-based materials on dehydrogenation performances of MgH_2. *J. of Alloys and Compd.*2015. Vol. 645.P. S509-S512.

69) DaryaniM., SimchiA., Sadati M., MdaahHosseiniH., TargholizadehH., KhakbizM.Effects of Ti-based catalysts on hydrogendesorption kinetics of nanostructured magnesiumhydride.*Int. J.of Hydrogen Energy*. 2014. Vol.39. P. 21007-210014; doi.org/10.1016/j.ijhydene.2014.10.078.

70) Rohit R. Shahi, Anand P. Tiwari, M.A. Shaz, O.N. Srivastava. Studies on de/rehydrogenation characteristics of nanocrystalline MgH_2 co-catalyzed with Ti, Fe and Ni. *Int. J. of Hydrogen energy*. 2013.Vol.38. P. 2778 – 2784;doi.org/10.1016/j.ijhydene.2012.11.073.

71) ZhangQ.A., ZhangL.X., WangQ.Q.Crystallization behavior and hydrogen storage kinetics of amorphousMg11Y2Ni2 alloy. J. Alloys Comp.2013. Vol. 551. P. 376–381; doi.org/10.1016/j.jallcom.2012.11.046

72) Andreas Schneemann, James L. White, ShinYoung Kang, Sohee Jeong, Liwen F. Wan,Eun Seon Cho, Tae Wook Heo, David Prendergast, Jeffrey J. Urban, Brandon C. Wood,Mark D. Allendorf, Vitalie Stavila. Nanostructured Metal Hydrides for Hydrogen Storage. *Chem. Rev.* 2018. Vol. 118, Nos. 22. P. 10775–10839; https://doi.org/10.1021/acs.chemrev.8b00313.

73) Rizo-Acosta Pavel, Fermı´n Cuevas, Latroche Michel. Optimization of TiH_2 content for fast and efficient hydrogen cycling of MgH2-TiH2 nanocomposites. *Int. J. of Hydrogen Energy*.2018. doi.org/10.1016/j.ijhydene.2018.04.169

74) Hui Yonga, Xin Weia, Yanhao Wanga, Shihai Guoa, Zeming Yuana, Yan Qia, Dongliang Zhaoa, Yanghuan Zhanga. Phase evolution, thermodynamics and kinetics property of transition metal (TM -Zr, Ti, V) catalyzed Mg–Ce–Y–Ni hydrogen storage alloys. J. of Physics and Chemistry of Solids. 2020. Vol. 144. P. 109516 - 109525;doi.org/10.1016/j.jpcs.2020.109516.

75) Akbarzadeh Fatemeh Zahra,Rajabi Mohammad. Mechanical alloying fabrication of nickel/cerium/MgH_2 nanocomposite for hydrogen storage: Molecular dynamics study and experimental verification. J. Alloys and Comps. 2022. Vol. 899. P. 163280-163289; doi.org/10.1016/j.jallcom.2021.163280

76) Sadhasivama T., Kimb Hee-Tak, Jungc Seunghun, Rohd Sung-Hee, Parka Jeong-Hun, Ho-Young Junga. Dimensional effects of nanostructured Mg/MgH_2 for hydrogen storage applications:A review Renewable and Sustainable Energy Reviews. 2017. v. 72. P. 523–534.doi.org/10.1016/j.rser.2017.01107.

77) Berezovets V.V., Denys R.V., ZavaliyI.Yu., KosarchynYu.V.. Effect of Ti-based nanosized additives on the hydrogen storage properties of MgH_2. Int. J. of Hydrogen Energy2022. Vol.47. Nos. 11. P. 7289-7298;doi.org/10.1016/j.ijhydene.2021.03.019.

78) Z. Min, Y. Lu, L. Ouyang and H. Wangm. Thermodynamic tuning of Mg-based hydrogen storage alloys. Materials, 2013. -Vol. 6. -p. 4654-4674.

79) ErshovaO.G., DobrovolskyV.D., SoloninYu.M.The role of Ni additive, size factor and surface chemicalstateindecreasing temperature and improving decomposition kinetics of the nanosized MgH_2hydride phase of mechanical alloys Mg +10wt.% Ni and MgH_2 +10wt.% Ni. Int. Independent Scientific Journal.2022. Vol. 1. Nos. 38. P. 22-32. https://doi.org/10.5281/zenodo.6559957.

80) Ershova O.G., DobrovolskyV.D., Khyzhun O.Yu., SoloninYu.M. XPS&TDS study of mechanism influence of surface & the addition Ti on thermal stability, kinetic of hydrogen desorption from MgH_2 received different methods. Physics and chemistry of solid state. 2011.Vol. 12. Nos.4.P. 1066-1073.

81) Dobrovolsky V.D., Khyzhun O.Y., Sinelnichenko A.K., Ershova O.G., Solonin Y.M. XPS study of influence of exposure to air on thermal stability and kinetics of hydrogen decomposition of MgH_2 films obtained by direct hydrogenation from gaseous phase of metallic. Journal of Electron Spectroscopy and Related Phenomena. 2017.- 215. - 28-35. http://dx.doi.org/10.1016/j.elspec.2017.01.001

82) Fermin Cuevas, Dmytro Korablov and Michel Latroche. Synthesis, structural and hydrogenation properties of Mg-rich MgH_2–TiH_2 nanocomposites prepared by reactive ball milling under hydrogen gasw. J. Phys. Chem. Chem. Phys., 2012, 14, 1200–1211. DOI: 10.1039/c1cp23030a.

83) Nicola Patelli, Marco Calizzi, Andrea Migliori, Vittorio Morandi, and Luca Pasquini. Hydrogen Desorption Below 150 °C in MgH_2–TiH_2Composite Nanoparticles: Equilibrium and Kinetic Properties. J. Phys. Chem. C 2017, 121, 21,11166–11177.doi.org/ 10.1021/acs.Jpcc.7b03169

84) LotoskyyM., DenysR., YartysV., EriksenJon, SergeJ. G., NyamsiN., CordelliaSita and CummingsF. An outstanding effect of graphite in nano-MgH_2-TiH_2 on hydrogenstorage performance. J. Mater. Chem. A. 2018, p. 1-16. DOI:10.1039/C8TA02969E.

85) Pavel Rizo-Acosta, Fermin Cuevas and Michel Latroche. Hydrides of early transition metals as catalysts and grain growth inhibitors for enhanced reversible hydrogen storage in nanostructured magnesium. *J. Mater. Chem. A*, 2019. 7. P. 23064 – 75. doi: 10.1039/C9TA05440E.

86) ShaoH., FelderhoffM., Sch¨uth F. and Cweidenthaler. Nanostructured Ti-catalyzed MgH_2 forhydrogen storage. Nanotechnology. 2011. 22. p. 235401. doi:10.1088/0957-4484/22/23/235401.

87) Hakan Gasan, Osman N. Celik, Nedret Aydinbeyli, Yasar M. Yaman. Effect of V, Nb, Ti and graphiteadditions on the hydrogen desorption temperature of magnesium hydride. Int. J. Hydrog.Energy. 2012. – 37. P.1912-1918.

88) 88. Chengshang Zhou, Zhigang Zak Fang, Pei Sun. An experimental survey of additives for improving dehydrogenation properties of magnesium hydride. Journal of Power Sources. 2015. – 278. p. 38 – 42.http://dx.doi.org/10.1016/j.jpowsour.2014.12.039.

89) 89. Dobrovolsky V.D., Radchenko O.G., Solonin Yu.M., Muratov V.B., I.A. Morozov. The influence of mechanical grinding on the thermal stability of the TiH_2 hydride. J. Metallofiz. Noveishie Tekhnol. 2006, v. 28, N.3. P. 303 – 311.

90) Dobrovolsky V.D., Ershova O.G., Solonin Yu.M., Khyzhun O.Yu. Hydrogen-sorption and thermodynamic characteristics of mechanically grinded $TiH_{1.9}$ as studied using thermal desorption spectroscopy. J. Alloys & Comp.2011. v.509, p. 128-133. doi:10.1016/j.jallcom.2010.09.003.