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The Influence of Complex Doping on Kinetics of Decomposition and Thermal Stability of Mg-Based Mechanical Alloys

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Mechanical alloys (MAs) were synthesized by the method of reactive mechanical alloying. At a hydrogen pressure of 0.1 MPa, with the use of thermal desorption spectroscopy, the thermal stability, the kinetics of hydrogen desorption from the hydride phase MgH_2 of the obtained MAs were studied. It has been established that the complex doping by of Fe, Si, Ti, leads to a significant improvement in the hydrogen desorption from the hydride phase MgH_2 of MA synthesized by the RMA. Hydrogen capacity C_H of MA after reactive grinding for 20 h. was found to be equal to 5.7 % wt. Due to this alloying, the decrease in the thermodynamic stability of MgH_2 is not established. The tested materials showed a high potential as hydrogen storage alloys especially for stationary application.

Keywords: mechanical alloy; hydrogen sorption properties; thermal stability; kinetics.

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Introduction

Hydrogen is a unique energy source having three times higher energy than traditional fuels. It is easy to be stored and transported; it can be very efficiently converted into electricity, for example, in fuel cells, while the only waste is water. The development of hydrogen energy promises a significant breakthrough in addressing such important issues as creating environmentally tolerant energy systems, reducing environmental pollution, improving energy security, developing infrastructure for road transport on hydrogen-oxygen fuel cells, etc.

Magnesium hydride-based materials have attracted significant attention. There exist a few magnesium alloys, the composites on its basis that are most promising in terms of the optimal combination of properties: high hydrogen capacity, relatively low hydrogen desorption temperature, high kinetic characteristics, acceptable cost. It is known that in order to use hydrogen permeation material in hydrogen storage systems on a car board the hydrogen capacity of 5 - 6 wt. % is needed. The decomposition temperature of the hydride phase is not higher than 150 - 200 °C.

Despite the attention of scientists to magnesium hydride, methods used for its production, studies of its properties, application of the hydride in the automotive industry (as a hydrogen-accumulating material) remains complicated due to high temperature (300 °C at 1 bar H_2) and slow kinetics of dissociation. The main problem is due to the necessity of decreasing the temperature of decomposition with simultaneous increase in its rate and preservation of the high hydrogen capacity and cyclic resistance of hydride phase MgH_2 of mechanical alloys to get a complex of required characteristics. Most often, the problem of simultaneous formation of several desired characteristics of MgH_2 is realized by the mechanical dispersion of commercial hydride in the presence of various catalytic admixtures (e.g., transition 3d- and 4d-metals [1-9] and their oxides and fluorides, intermetallic compounds, and admixtures of the nontransition metals, such as Al, Cu, Zn, In, and Sn, graphite, etc.) or by the procedure of grinding of powders of metallic Mg with these admixtures in hydrogen or in atmospheres of inert gases with subsequent hydrogenation from the gas phase [1-31].

In order to decrease the thermodynamic stability

of MgH_2 , it is conventional to use mechanical alloys in the form of solid solutions in magnesium of one or several metals capable of decreasing the enthalpy of formation/decomposition of $\text{Mg}(\text{Me})\text{H}_2$ [32-39]. According to the theoretical predictions [5], the hydrides of solid solutions of Al, Ti, Fe, Ni, Cu, and Nb in magnesium should have lower enthalpies of formation and decompose at temperatures lower than that of pure MgH_2 . It was shown that the thermodynamic stability of these hydrides of solid solutions depends on the procedures and conditions of their production [32-36]. Thus, the decomposition of the hydride phase $\text{Mg}(\text{In})\text{H}_2$ of the mechanical alloy obtained as a result of high-energy grinding of a powder of MgH_2 with 10 at. % In in hydrogen under a pressure of 150 bar originates at 262.3°C under a hydrogen pressure of 1 bar in the reactor [35]. At the same time, the analysis of the PCT (pressure-composition-temperature) curves [35] for the hydride of a solid solution of aluminum in magnesium formed by grinding a mixture of 90 at. % MgH_2 with 10 at. % Al in hydrogen under a pressure of 150 bar does not reveal the indicated effect of destabilization of the hydride phase $\text{Mg}(\text{Al})\text{H}_2$ during dehydrogenation. In [39-44], silicon was used to destabilize MgH_2 hydride. Silicon forms relatively strongly bound compounds with Mg (Mg_2Si forms upon dehydrogenation of MgH_2 for the MgH_2/Si system) that reduces dehydrogenation enthalpies and increases equilibrium hydrogen pressures. Calculations using tabulated thermodynamic parameters predict an equilibrium pressure of 1 bar at approximately 20 °C and 100 bar at approximately 150 °C. However, the kinetics at 150 °C are too slow for direct hydrogenation /dehydrogenation. The possibility of increasing the solid-state reaction rate of MgH_2 with Si by modifying the mixture preparation method and adding chemical elements or compounds, such as Ti, Ni, NbF_5 , TiO_2 , Cr_2O_3 , was investigated in [40, 42]. It has been shown that these catalysts can effectively speed up the destabilization reaction at the beginning.

In this article with the aim of lowering the temperature, improvement of the kinetics of the decomposition of stoichiometric MgH_2 hydride, the possibility of its complex doping by Si, Ti, Fe using the method of reactive mechanochemical alloying (RMA) has been investigated. A number of mechanical alloys-composites (MAs) of Mg with additions of a different composition of titanium, iron and silicon were synthesized. The phase composition, hydrogen sorption properties, thermal stability and desorption kinetics of hydrogen, microstructure have been investigated employing the X-ray diffraction (XRD), thermodesorption spectroscopy (TDS), scanning electron microscopy (SEM) methods.

For comparison, we synthesized an additional composite alloy in the same condition that were used for obtaining the MAs samples, without any additives. Choosing Ti and Fe, we take into account the fact that these transition metals have catalytic properties. In the course of reactive mechanical fusion, they may improve significantly the kinetics of hydrogenation of magnesium playing the role of dispersing agents and noticeably affect the thermodynamic stability of the

MgH_2 phase formed in the course of synthesis according to the theoretical prediction [5]. In order to destabilize MgH_2 , silicon is also included in the additive composition.

I. Experimental part

The mechanical alloys-composites has been synthesized by reactive grinding in hydrogen of powders: Mg + 5 wt. % Si + 5 wt. % Ti + 2 wt. % Fe (further MA1), Mg + 5 wt. % Si + 5 wt. % Fe + 2 wt. % Ti (MA2), Mg + 10 wt. % Si + 2 wt. % Ti + 2 wt. % Fe (MA3), pure MgH_2 (MA4). The main aim of this study was to obtain the above mentioned MA1-MA4 mechanical alloys and explore the processes of hydrogen desorption 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. 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 was also studied. The selected alloying elements influence on MgH_2 decomposition kinetics was the aim of the investigation as well

The commercial powders of Mg, Ti, Fe, Si with a purity of 99.98 % and particles sizes of 100; 3; 6,7; 10 μm , respectively, have been used as raw materials. The mechanical fusion by reactive grinding of the mixture of powders of MA1-MA4 composition, was realized in a RETCH100 ball mill with steel balls in a hydrogen atmosphere (under a hydrogen pressure of 1 MPa, for a velocity of rotation of 450 rot/min and a duration of grinding of 20 h). The ratio of the metallic balls mass and the treated mixture of powders was 20:1. Milling was interrupted every 50 min to allow the vial to cool down to room temperature followed by the monitoring of the current state of hydrogen absorption. We use one and the same conditions of synthesis for all MAs under consideration that allows making a proper comparison of different alloying elements effect on temperature and the kinetics of MgH_2 hydride phase decomposition of synthesized MAs. Conditions of synthesis of all MA samples derived by direct hydrogenation from the gas phase were also the same. After the MA synthesis and obtaining the first hydrogen desorption curve, the sample was not removed from the reactor. At temperature of 400 °C the reactor was filled with hydrogen until hydrogen pressure was 6 MPa and during 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. For the X-ray phase diffraction analysis of specimens, we used a DRON-3M diffractometer. The X-Ray patterns were obtained employing $\text{CuK}\alpha$ -radiation with a graphite monochromator. The profiles of diffraction lines were plotted with scanning steps of 0.1° and with exposure at each point of the spectrum over 20 sec. The diffraction

patterns were analyzed using fullprof software Powder Cell 2.4 ([https:// powdercell-for-windows. software. informer. com /2.4/](https://powdercell-for-windows.software.informer.com/2.4/)).

By the method of thermal desorption spectroscopy with a computerized automatic installation, we studied the influence of alloying elements on the hydrogen sorption properties, thermal resistance, the kinetics of hydrogen desorption from the MgH₂ hydride phase. This

installation allows to plot the isobars of desorption / resorption of hydrogen under various pressures in the reactor and to perform the hydrogenation / dehydrogenation of specimens under pressures up to 10 MPa and temperatures being in the range from room temperature to 1200 °C. The details are presented in Refs. [29].

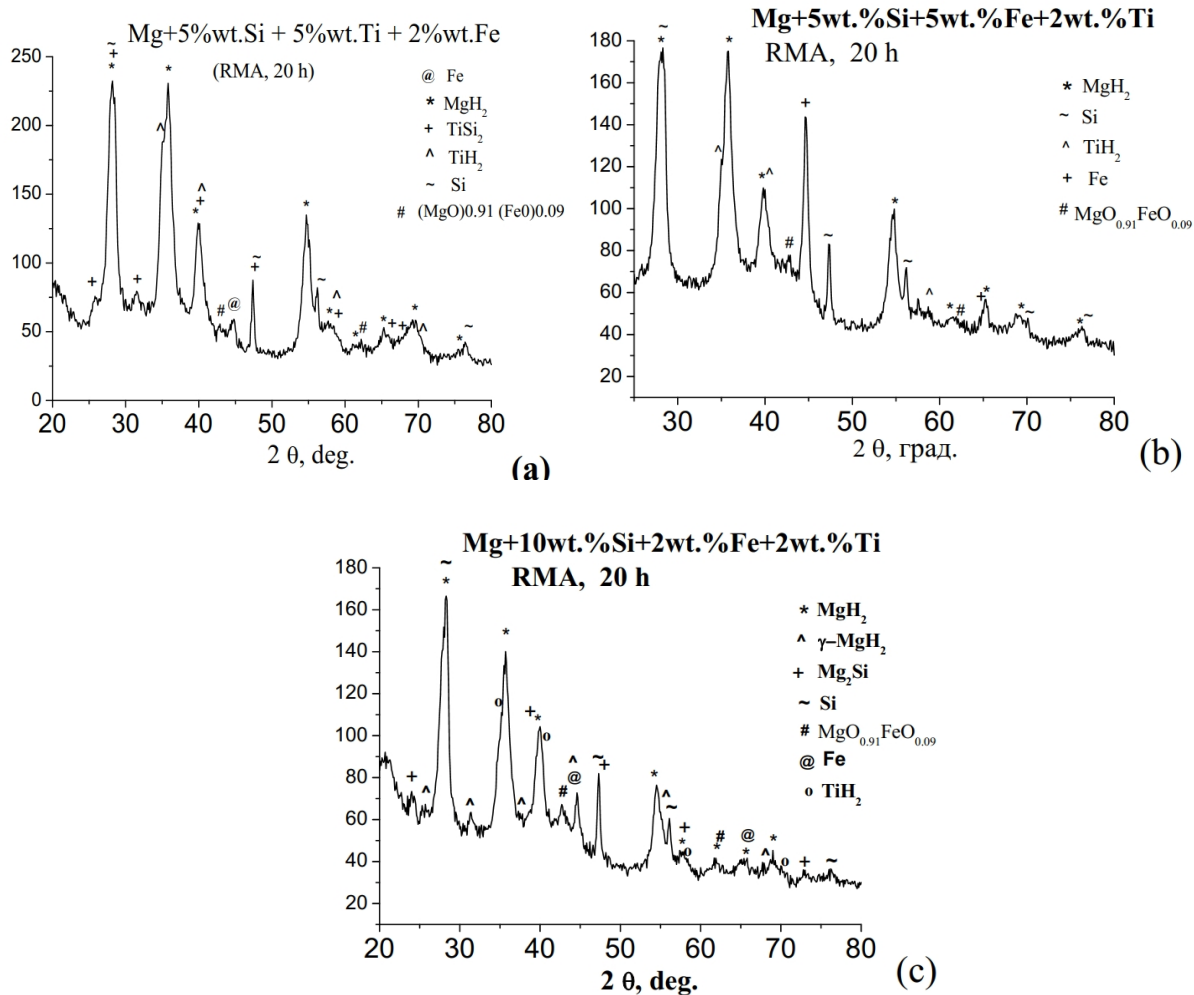


Fig. 1. X-ray diffraction pattern of specimens of the mechanical alloys: a - MA1, b - MA2, c - MA3 obtained by reactive mechanical alloying.

Table 1

Phase compositions and properties of MA in the case of its first heating after RMA and of its first hydrogenation from the gaseous phase (HGM)

Mechanical alloy-composite wt. %	Phase compositions		D _{part.} μm
	RMA	HGM	RMA
MA1 (Mg + 5 Si + 5 Ti + 2 Fe)	Fe, Si, MgH ₂ , TiSi ₂ , TiH ₂ , MgO _{0,91} FeO _{0,09}	Fe, Si, MgH ₂ , TiH ₂ , MgO _{0,91} FeO _{0,09} after 8hydr.	0,6
MA2 (Mg + 5 Si + 5 Fe + 2Ti)	Fe, Si, MgH ₂ , TiH ₂ , MgO _{0,91} FeO _{0,09} .	Fe, MgH ₂ , MgO ₂ , Mg ₂ Si after 4hydr.	0,4
MA3 (Mg + 10 Si + 2 Fe + 2 Ti)	Fe, Si, MgH ₂ , γ- MgH ₂ , Mg ₂ Si, TiH ₂ , MgO _{0,91} FeO _{0,09}	Fe, MgH ₂ , Mg ₂ Si, TiH ₂ , MgO _{0,91} FeO _{0,09} after 5 hydr.	0,3
MA4	Mg, MgH ₂ , MgO _{0,91} FeO _{0,09}	Mg, MgH ₂ , MgO _{0,91} FeO _{0,09}	0,7

II. Results and discussion

2.1. XRD analysis and SEM characterization of the samples.

Fig. 1 shows XRD pattern of the MA1-MA3 samples derived by reactive mechanical alloying (RMA) and Fig.2 - after the gas phase hydrogenation (GPH) mechanical alloys. The information on the phase composition of the MA specimens obtained by RMA and after GPH is presented in Table 1. As Table 1 shows, all mechanical alloys (MA1-MA3) are composites, as a result of reactive mechanical alloying. In addition to MgH_2 , they contain Si, Fe phases, as well as new crystalline phases which are not parts of the initial mixture of mechanical alloys powders and are magnesium oxides, magnesium compounds with alloying elements (Mg_2Si in the case of MA3) and compounds TiH_2 and $TiSi_2$. After the first hydrogenation / dehydrogenation cycles from the gas phase, all MAs reveal changes in the composite phase composition. In the case of MA1, Ti_2Si phase is already absent, in the case of MA2 and MA3, Mg_2Si phase appeared instead of the pure-silicon phase. The parameters of crystal lattices and volume of unit cells for β - MgH_2 hydride phase of MAs (Table 2) have been determined by the full-profile Rietveld method using Powder Cell 2.4 program.

Fig. 3 shows the microstructure and morphology of

Table 2
Crystal structure data (unit cell parameters: a, c - Å; V - Å³) for MgH_2 Hydride phase composites

Mechanical alloy-composite, wt. %	Unit cell parameters
MA1 (Mg + 5 Si + 5 Ti + 2 Fe)	a = 4.5011 V= 2.025 c = 3.0413
MA2 (Mg + 5 Si + 5 Fe + 2 Ti)	a = 4.5148 V= 1.616 c = 3.0430
MA3 (Mg + 10 Si + 2 Fe + 2 Ti)	a = 4.5123 V= 61.2557 c = 3.0345
MA4	a = 4.5223 V= 61.684 c = 3.0157

the three above mentioned MAs. It is well seen that after mechanical dispersion, the powders represent a mixture of particles with their sizes from 0.1 to 0.8 μm and agglomerates with sizes from 2 to 5 μm . Based on our experimental data, the average particle size, which in turn consists of nanorods (the average size is 9-12 nm) in MA1, MA2, MA3 is 0.6, 0.4, 0.3 μm respectively. After repeated hydrogenation/dehydrogenation of powders from the gas phase, as shown by the study of their

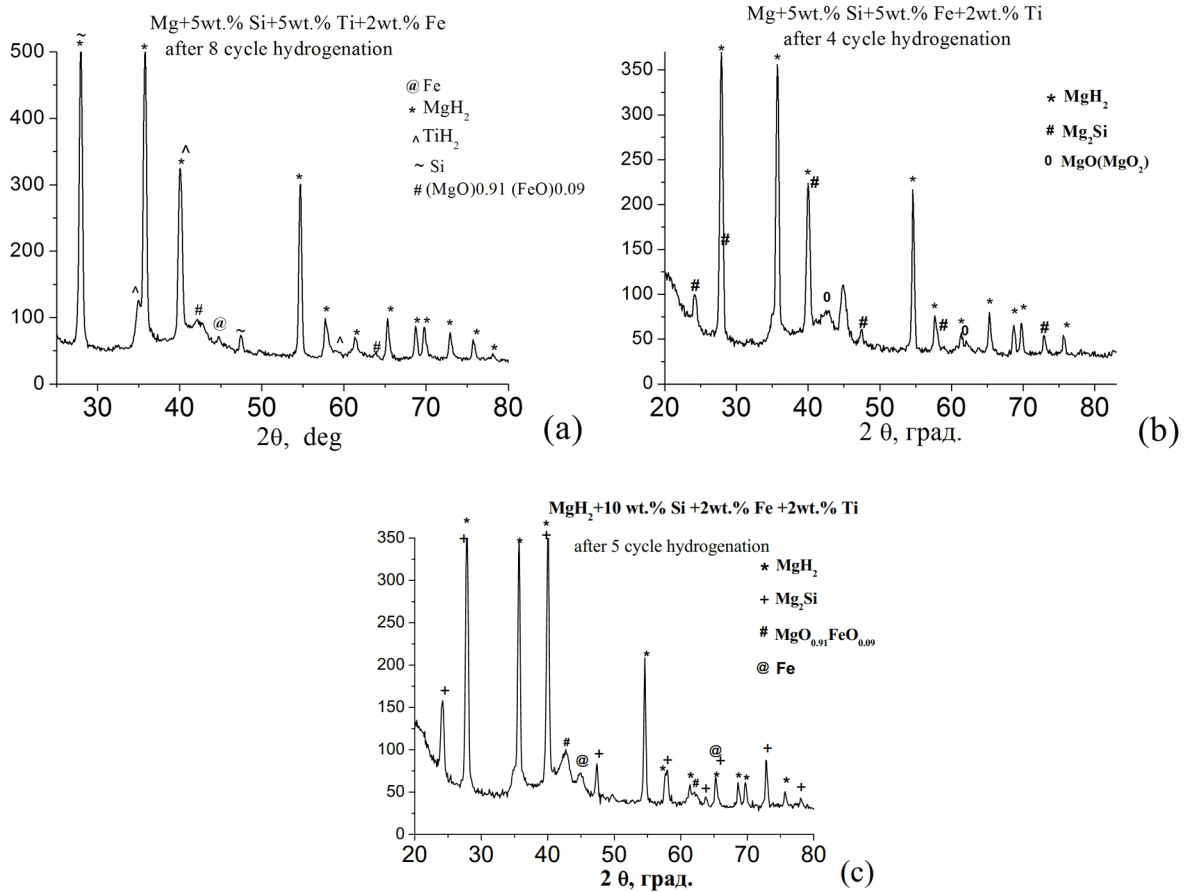


Fig. 2. X-ray diffraction pattern of specimens of the mechanical alloys after hydrogenation from the gaseous phase: a - MA1, b - MA2, c - MA3.

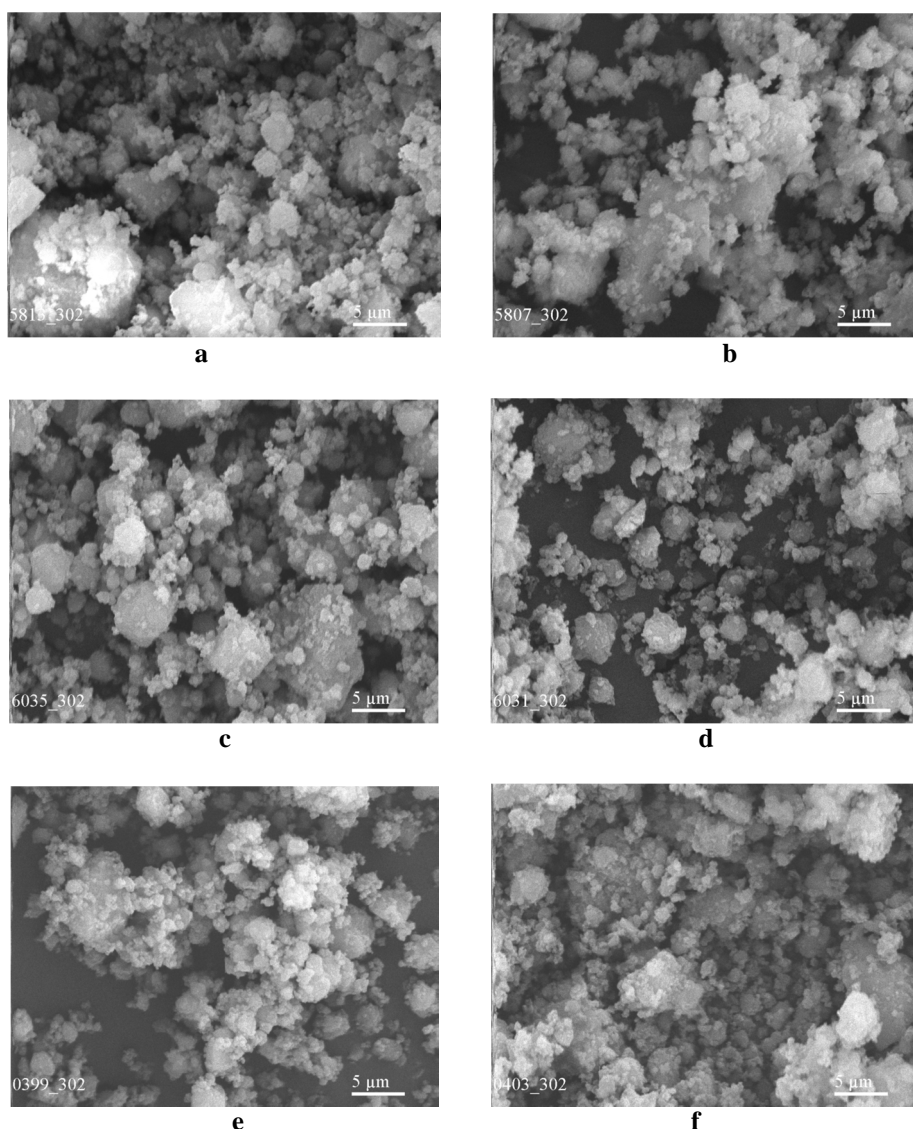


Fig. 3. Microstructures of mechanical alloys: a, b - Mg + 5 wt.% Si + 5 wt.% Ti + 2 wt.% Fe; c, d - Mg + 5 wt.% Si + 5 wt.% Fe + 2 wt.% Ti; e, f - Mg + 10 wt.% Si + 2 wt.% Fe + 2 wt.% Ti. a, c, e - after synthesis by RMA method 20 h.; b, d, f – after first cycles of hydrogenation from the gas phases.

microstructure, the average particle size decreases (Fig. 3b) and the average grain size increases to 50 - 70 nm due to cyclic heating/cooling. These data correlate with the data of the X-ray phase analysis. Comparing the diffraction reflexes of the MA sample prior and after its cycling, one can observe, in the latter case, their noticeable narrowing (Fig. 1 and Fig. 2).

Comparing the microstructure of all mechanical alloys with different content of Si, Ti, Fe admixtures, it can be seen that the powders after the RMA have irregularly shaped particles agglomerated together with typical morphology of powdery structures. There is a wide distribution of particles in sizes ranging from 0.1 to 0.8 μm . It has been established that the uniformity of the particles in size increases for samples with a high content of silicon. The content of particles with an average size of 0.1 - 0.5 μm in an alloy of 10 wt. % Si is 70 % (Fig. 3, e, f), while in alloys with 5 wt. % Si the content of such particles is approximately 30 % (Fig. 3, a-d). Silicon in composites in the process of grinding helps to grind the particles of the formed magnesium hydride due to its

natural strength. In powders of an alloy of 10 wt. % Si after the first cycles of their hydrogenation/dehydrogenation (Fig. 3,f), there is a smaller quantity of large agglomerates, while in samples of mechanical alloys with 5 wt. % Si (Fig. 3,b, d) the quantity of such agglomerates is bigger.

2.2. Thermal behavior of the mechanical alloys-composites

Hydrogen desorption isobars of the MA1-MA4 samples at their first heating after RMA synthesis are shown in Fig. 4, and those recorded for the samplers after first hydrogenation from the gas phase are presented in Fig. 5. 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 was 3 $^{\circ}\text{C}/\text{min}$. The mass of samples of all MAs was 0.15 g. The isobars shown in Fig. 3 and Fig. 4 were used to determine the beginning temperature ($T_{\text{beg.}}$) of hydrogen desorption from hydride phase MgH_2 of MA1-MA4 and their hydrogen

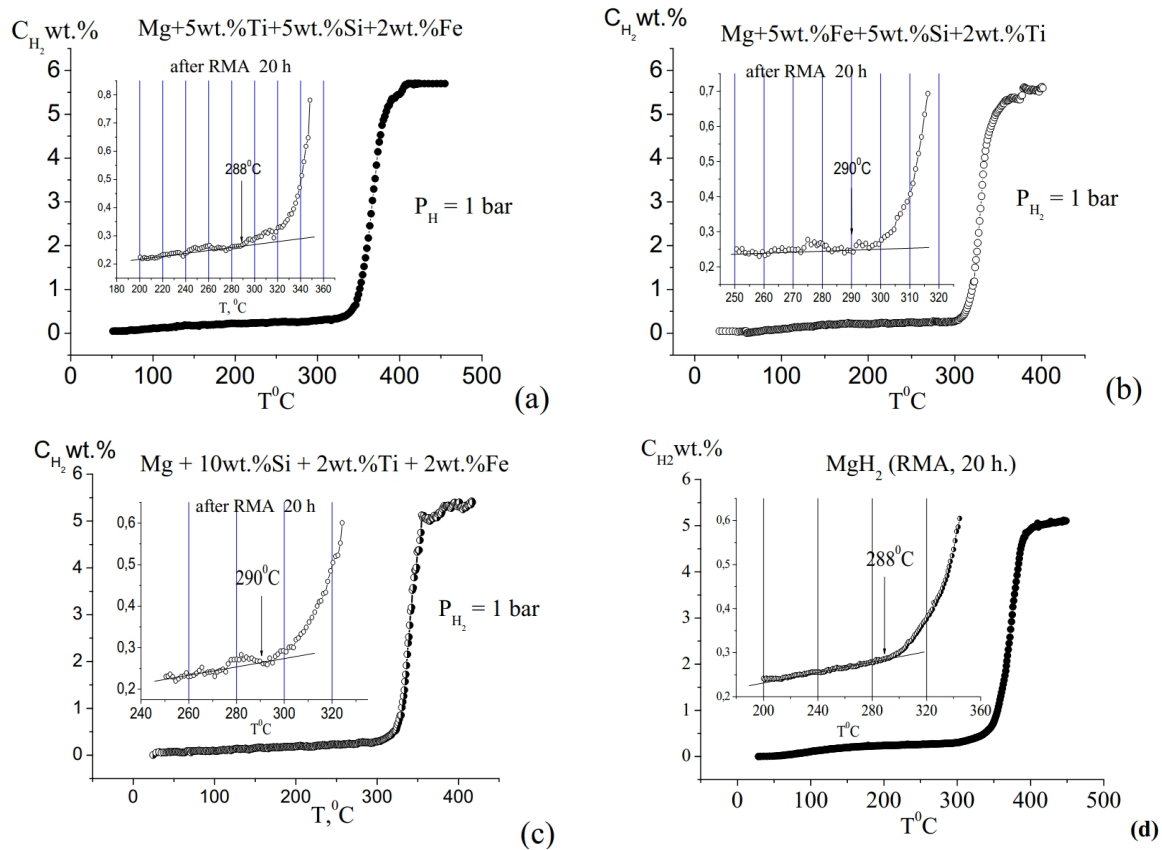


Fig. 4. Isobars of hydrogen desorption ($P_{H_2} = 0.1$ MPa) from the hydride phase MgH_2 of the mechanical alloys in the case of its first heating (after reactive mechanical alloying for 20h): a – MA1; b – MA2; c – MA3; d – MA4.

Table 3

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

Mechanical alloy-composite, wt. %	1-st desorption after RMA		1-st desorption after HGM	
	$T, ^\circ C$	$C_{H_2}, wt. \%$	$T, ^\circ C$	$C_{H_2}, wt. \%$
MC1(Mg + 5Si + 5Ti+2Fe)	288	5.7	288	5.3
MC2 (Mg + 5Si + 5Fe+2Ti)	288	5.6	310	5.5
MC3 (Mg +10Si +2Fe+2Ti)	290	5.4	310	4.1
MC 4 (MgH_2)	288	5.1	320	6.3

capacities. The obtained data are shown in Table 3. After obtaining the curves of the first desorption of hydrogen from the MA samples shown in Figure 4, the samples were not removed from the reactor. At 400 °C, hydrogen pressure of 6 MPa was in the reactor. During the sample cooling together with the furnace its first (and subsequent) hydrogenation from the gas phase took place. From Figs. 4 and 5 and Table 3, it is obvious that the temperature of the beginning of hydrogen release from the hydride phase MgH_2 of MA1, MA2, MA3 composites after RMA was 288, 290, 290 °C, respectively. After their first hydrogenation from the gas phase, the temperature was 288, 313, 310 °C, respectively. If one compares T_{beg} of the release of hydrogen from the unalloyed MgH_2 phase of MA4

(288 °C) with the same temperature for MA1, MA2, MA3, one can states that the addition of Si, Ti and Fe to magnesium practically does not reduce the thermal stability of MgH_2 of all MAs and, consequently, does not reduce the temperature of the beginning of hydrogen desorption. In our opinion, the explanation of this can be the fact that in the conditions of our method of obtaining of MAs does not form a solid solution in magnesium Si, Ti, Fe, whose hydride is $Mg(Si, Ti, Fe)H_2$, according to [5], should have a lower formation enthalpy and a lower thermodynamic stability and decomposition temperature of MgH_2 . The evidence of the fact that $Mg(Si, Ti, Fe)H_2$ hydride was not derived (or its quantity is rather minor) can be, in accordance with the XRD data (see Table 1), the presence in the composite of TiH_2 and a significant

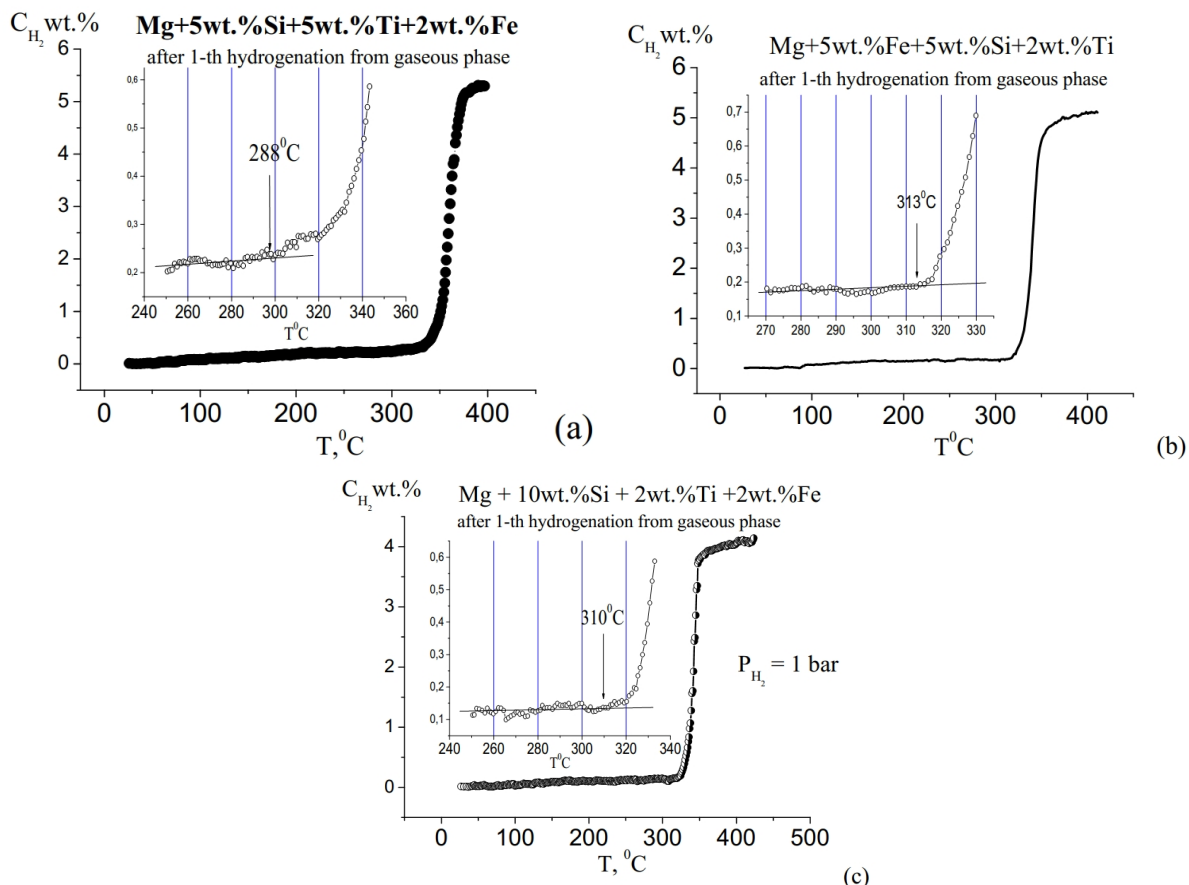


Fig. 5. Isobars of hydrogen desorption from the MgH_2 hydride phase of the mechanical alloys after their first hydrogenation from the gaseous phase (for a heating rate of $3^\circ\text{C}/\text{min}$ under a hydrogen pressure of 0.1 MPa): a – MA1; b – MA2; c – MA3.

Table 4

Time (min.) of desorption of half ($\tau_{1/2}$) and full (τ_f) hydrogen amount from MgH_2 hydride phase at 310°C and 330°C

Mechanical alloy-composite, wt. %	310°C		330°C	
	$\tau_{1/2}$	τ_f	$\tau_{1/2}$	τ_f
MA1 (Mg + 5 Ti+5 Si+ 2 Fe)	45	90	14	30
MA2 (Mg+5 Si+5 Ti+2 Fe)	25	48	12	28
MA3 (Mg+10 Si+2 Ti+2 Fe)	11,5	20	6,3	10
MA 4 (MgH_2)	88	130	31	75

content of pure Si and Fe phases (the latter phases are formed due to substantial amounts of the alloying elements Si, Ti and Fe). As can be seen from Table 2, the absence of the expected decrease in volume of the unit cell of hydride phase MgH_2 of the composites MA1, MA2, and MA3 compared with that of the same hydride phase of the composite MA4 can also be an indication of the absence of formation in our synthesis conditions of $\text{Mg}(\text{Si}, \text{Ti}, \text{Fe})\text{H}_2$ hydride. From data listed in Table 3, it is worth noting a decrease of hydrogen capacity in the composites MA1, MA2, and MA3 after their hydrogenation from the gas phase. In the case of the composites MA2 and MA3, a slight increase in the temperature of the beginning of hydrogen desorption

from 290°C to 310°C and MA4 to 320°C . In our opinion, the mentioned increase in temperature may be caused by the absence of a phase of pure silicon, which possesses the effect of destabilization of MgH_2 and contributes to a decrease in the decomposition temperature, and a significant increase in the amount of Mg_2Si phase in the composites MA2 and MA3 after their hydrogenation from the gas phase. It should be noted that as a result of 4 - 10 cycles of hydrogenation / dehydrogenation of the composites MA1, MA2 and MA3 from the gas phase, we did not observe significant changes in the nature of the desorption curves and their position in the temperature scale. This may indicate reversibility of the process of cyclic hydrogenation / dehydrogenation of the obtained MAs and the absence of significant degradation of their hydrogen adsorption properties.

2.3. Mechanical alloys hydrogen desorption kinetics process

Hydrogen desorption kinetics from MgH_2 hydride phase of all MAs after their hydrogenation from the gas phase under the same conditions has been investigated at 310°C and 330°C . Hydrogen desorption kinetic curves are presented in Fig. 6. All curves 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 ($\tau_{1/2}$) and total hydrogen quantity (τ_f) for all

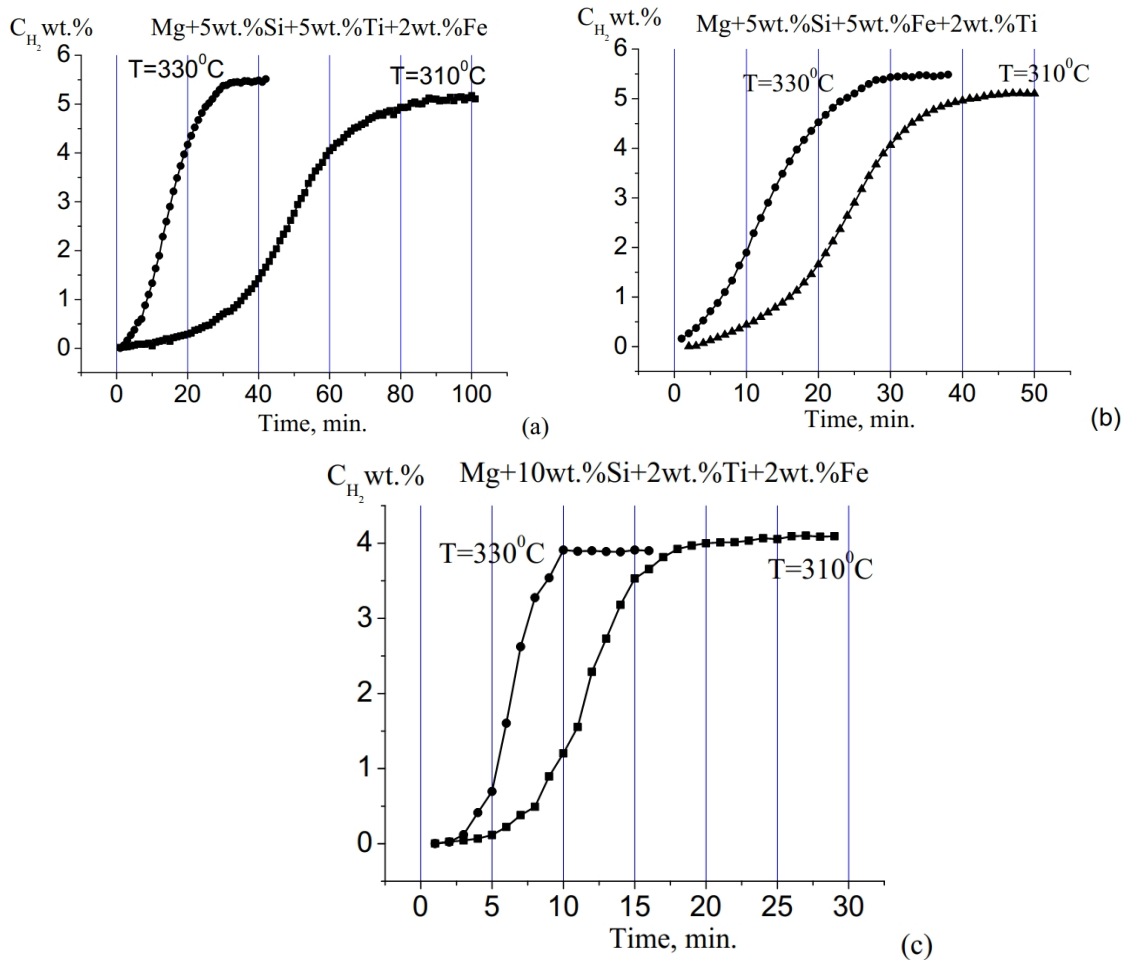


Fig. 6. Kinetic curves of hydrogen desorption at temperature 310 and 330 °C from the MgH_2 hydride phase of the mechanical alloys: a – MA1; b – MA2; c – MA3; d – MA4.

MAs are shown in Table 4. As we can see from Table 4 and kinetic curves presented in Fig. 6, MA3 mechanical alloy-composite has the best kinetics of hydrogen desorption from MgH_2 . The composite MA1 possesses the worst kinetics. If one compare the kinetic curves of the composites MA1, MA2 and MA3 presented in Figs. 6, a-c with the kinetic curve of MA4 (Fig. 6d), one can see a significant difference in time that is necessary for the release of all hydrogen at temperature of 330 °C. The comparison shows that the addition of Si, Ti and Fe to magnesium significantly improves the kinetics of hydrogen desorption from hydride phase MgH_2 in all MAs, and the fast process of hydrogen desorption has been provided by the addition 10 wt. % Si + 2 wt. % Ti + 2 wt. Fe. In our opinion, Fe and Ti play the main role in improving the kinetics of hydrogen desorption in the composites MA1 and MA2. They possess high catalytic properties and favor recombination of hydrogen on the particle surface of the hydride phase, and, consequently, reduce its thermal stability. Si plays a significant role also in improving the kinetics of the process of hydrogen desorption in MA3, whose content in the addition to Mg 5 times higher than the contents of titanium or iron. Silicon does not possess such high catalytic properties as titanium and iron and does not affect the chemical state of the particle surface as Ti and Fe. However, in the process of reactive grinding silicon acts as an effective

dispersive element and it helps to reduce the average grain size of hydride phase MgH_2 of the MAs, and, as a result, improves the kinetics of hydrogen desorption process. Confirmation of such conclusion can be the results of microstructure studies of all MAs. The smallest average grain size of the hydride phase MgH_2 is detected in MA3, where the content of silicon is the highest, and the kinetics of the hydrogen desorption process is the best (Tables 1 and 4).

Conclusion

The new alloys-composites with reduced thermal stability and improved kinetics of the decomposition of their hydride phase MgH_2 were synthesized by the reactive grinding in the hydrogen atmosphere of a mixture of Mg powder with different content of additives Ti, Fe and Si. The influence of alloying elements Si, Ti, Fe on the hydrogen sorption properties, thermal stability and kinetics of the hydrogen desorption process from the hydride phase MgH_2 of the obtained MAs has been studied. It was established that the addition of Ti, Fe and Si to magnesium leads to a significant improvement in the kinetics of hydrogen desorption from the hydride phase MgH_2 of the obtained MAs, as evidenced by the experimentally recorded significant reduction in time of

the half and total quantity of desorbed hydrogen. The reduction of the thermodynamic stability of MgH₂ hydride due to its doping by Si, Ti, and Fe was not detected. Results of the present study can be used in the development of new hydrogen sorbent materials for hydrogen energy.

Conflict of interest

The authors confirm that this article content has no conflict of interest. All authors have approved the final article.

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- [1] A. Bassetti, E. Bonetti, L. Pasquini, A. Montone, J. Grbovic, V. Antisari, J. Eur. Phys. B 43, 19 (2005) (doi: 10.1140/epjb/e2005-00023-9.)
- [2] J.-L. Bobet, E. Akiba, B. Darriet, Int. J. Hydrogen Energy 26, 493(2001) (doi:10.1016/S0360-3199(00)00082-3).
- [3] S.-N. Kwon, S.-H. Baek, R. D. Mumm, S.-H. Hong, M.-Y. Song, Int. J. Hydrogen Energy 33, 4586 (2008) (doi:10.1016/j.ijhydene.2008.05.097).
- [4] J. Mao, Z. Guo, X. Yu, H. Liu, Z. Wu, Int. J. Hydrogen Energy 35, 4569 (2010) (doi: 10.1016/j.ijhydene.2010.02.107).
- [5] C.X. Shang, M. Bououdina, Y. Song, Z.X. Guo, Int. J. Hydrogen Energy 29, 73 (2004) (doi:10.1016/S0360-3199(03)00045-4).
- [6] O.G. Ershova, V.D. Dobrovolsky, Yu.M. Solonin, O.Yu. Khyzhun, A.Y. Koval, J. Alloys Compound 464 212 (2008) (doi:10.1016/j.jallcom.2007.10.064).
- [7] O. Ershova, V. Dobrovolsky, R. Morozova, Yu. Solonin, Hydrogen Materials Science and Chemistry of Carbon Nanomaterials (T.N. Veziroglu (Ed.), Springer, Dordrecht, 2007).
- [8] O. Ershova, V. Dobrovolsky, Yu. Solonin, Carbon Nanomaterials in Clean Energy Hydrogen Systems (B. Baranowski (Ed) Springer Science + Business Media B.V., 2008).
- [9] R.Sh. Rohit, P.T. Anand, M.A. Shaz, O.N. Srivastava, Int. J. Hydrogen Energy 38, 2778 (2013) (doi:10.1016/j.ijhydene.2012.11.073).
- [10] Z. Degouche, J. Goyette, T.K. Bose, R. Schulz, Int. J. Hydrogen Energy 28, 983 (2003) (doi.org/10.1016/S0360-3199(02)00196-9).
- [11] J. Huot, J.F. Pelletier, L.B. Lurio, M. Sutton, R. Schulz, J. Alloys Compound 348, 319(2003) (doi:10.1016/S0925-8388(02)00839-3).
- [12] W. Oelerich, T. Klassen, R. Borman, J. Alloys Comp. 315, 237(2001) (doi.org/10.1016/S0925-8388(00)01284-6).
- [13] Xi Chen, Jianxin Zou, Shuqing Huang, He Guangli, Ning Zhao, Xiaoqin Zeng, Wenjiang Ding, RSC Adv. 8, 18959 (2018) (doi: 10.1039/c8ra01963k).
- [14] E. David, J. Achiev. Mat. Manufact. Eng. 20, 87 (2007).
- [15] V.D. Dobrovolsky, O.G. Ershova, Yu.M. Solonin, O.Y. Khyzhun, V. Paul-Boncour, J. Alloys Comp. 465, 177 (2008) (doi:10.1016/j.jallcom.2007.10.125).
- [16] M. Polanski, J. Bystrzycki J. Alloys Compd. 486, 697 (2009) (doi:10.1016/j.ijhydene.2009.06.02).
- [17] J.-C. Crivello, B. Dam, R.V. Denys, M. Dornheim, D.M. Grant, Appl.Phys. A 122, 97 (2016) (doi:10.1007/s00339-016-9602-S).
- [18] T. Sabitu, G. Gallo, A.J. Goudy, J. Alloys Compd. 499, 35(2010) (doi:10.1016/j.Jallcom.2010.03.128).
- [19] M. Tian, C. Shang J. Chem. Technol. Biotechnol. 86, 69 (2011) (doi:10.1002/jctb.2479).
- [20] M. Sherif El-Eskandarany, H.S. AlMatrouk, Ehab Shaban, Ahmed Al-Duweesh, Materials Today: Proceedings 3, 2608(2016).
- [21] C.X. Shang, Z.X. Guo J.Power Sources 129, 73 (2004) (doi:10.1016/j.jpowsour.2003.11.013).
- [22] S.N. Klyamkin, B.P. Tarasov, E.L. Straz, R.V. Lukashev, I.E. Gabis, E.A. Evard, A.P. Voyt, Int. Sci. J. Alternat. Energy Ecol. 1 (21), 27 (2005).
- [23] T. Spassov, V. Rangelova, P. Solsona J. Alloys Compd. 398, 139 (2005) (doi:10.1016/j.jallcom.2005.02.035).
- [24] P. Delchev, P. Solsona, B. Drenchev, J. Alloys Compd. 388, 98 (2005)103 (doi:10.1016/j.Jall com. 2004.07.001).
- [25] A. Ming, Mater. Sci. Eng. B 117, 37(2005) (doi:10.1016/j.mseb.2004.10.017).
- [26] A. Montone, J. Grbovič, A. Bassetti Int. J. Hydrogen Energy 31, 2088 (2006) (doi: 10.1016/j.ijhydene.2006.01.020).
- [27] Z.G. Huang, Z.P. Guo, A. Calka, J. Alloys Compd. 427, 94 (2007) (doi:10.1016/j.jallcom.2006.03.069).

- [28] M.A. Lillo-Ródenas, Z.X. Guo, K.F. Aguey-Zinsou, Carbon 46, 126 (2008) (doi:10.1016/j.carbon.2013.01.058).
- [29] O.G. Ershova, V.D. Dobrovolsky, Yu.M. Solonin, O.Yu. Khyzhun, A.Yu. Koval, Materials Chemistry and Physics 62, 408 (2015) (doi:10.1016/j.matchemphys.2015.06.007).
- [30] K.G. Bambhaniya, G.S. Grewal, V. Shrinet, N.L. Sindh, T.P. Govindan, Int. J. Hydrogen Energy 37, 3671 (2012) (doi:10.1016/j.ijhydene.2011.04.099).
- [31] O.G. Ershova, V.D. Dobrovolsky, Yu.M. Solonin, Fiz. Khim. Tverd. Tila 14 (1), 101 (2013).
- [32] M. Bououdina, Z.X. Guo, J. Alloys Comp. 336, 222 (2002) (doi:10.1016/S0925-8388(01)01856-4).
- [33] M. Tanniru, D.K. Slattery, F. Ebrahimi, Int. J. Hydrogen Energy 35, 3555 (2010) (doi:10.1016/j.ijhydene.2010.01.109).
- [34] M. Tanniru, D.K. Slattery, F. Ebrahimi, Int. J. Hydrogen Energy 36, 639 (2011) (doi:10.1016/j.ijhydene.2010.09.083).
- [35] C. Zhou, Z. Z. Fang, J. Lu, X. Luo, C. Ren, P. Fan, Y. Ren, and X. Zhang, J. Phys. Chem. C118, 11526 (2014) (doi:10.1021/jp501306w).
- [36] S. Bouaricha, L.P. Dodelet, D.Guay, J.Huot, S.Boily, R.Schulz, J. Alloys Compd. 297, 282 (2000) doi:10.1016/S0925-8388(99)00612-X.
- [37] J.F. Stampfer, C.E. Holley, J.F. Suttle, J. Amer. Chem. Soc. 82, 3504 (1960) (doi:10.1021/ja01499 a006).
- [38] O.G. Ershova, V.D. Dobrovolsky, O.Yu. Khyzhun, Yu.M. Solonin, Physics and chemistry of solid state 12 (4), 1044 (2011).
- [39] John J. Vajo, J. Phys. Chem. B 108, 13977 (2004) (doi:10.1021/jp040060).
- [40] M. Polanski, J. Bystrzycki, Int. J. Hydrogen Energy 34, 7692 (2009) (doi:10.1016/j.ijhydene.2009.06.002).
- [41] D.A. Paskevicius, A. Sheppard, C.J. Chaudhary, C.J. Webb, E. Mac, A. Gray, H.Y. Tian, V.K. Peterson, E. Buckley, J. of Hydrogen Energy 36, 10779 (2011) (doi:10.1016/j.ijhydene.2011.05.132).
- [42] Motoki Shimada, Hisashi Tamaki, Eiji Higuchi, J. of Materials and Chemical Engineering Jul. 2(3), 64 (2014).
- [43] Anna-Lisa Chaudhary, M. Paskevicius, D.A. Sheppard, J. Alloys Compd. 623, 109 (2015) (doi.org/10.1016/j.jallcom.2014.10.086).
- [44] J. Crivello, R.V. Denys, M. Dornheim, M. Felderhoff, D.M. Grant, J. Huot, T.R. Jensen, P.De Jongh, M. Latroche, G.S. Walker, C.J. Webb, V.A. Yartys, Appl. Phys. A 122, 85 (2016) (doi:10.1007/s00339-016-9601-1).

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Вплив комплексного легування на кінетику розкладу та термічну стабільність механічних сплавів на основі Mg

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Механічні сплави (МС) були синтезовані методом реактивного механічного сплавлення. При тиску водню 0,1 МПа з використанням термодесорбційної спектроскопії були вивчені термостабільність, кінетика десорбції водню з гідридної фази MgH_2 отриманих МС. Встановлено, що комплексне легування Fe, Si, Ti призводить до значного поліпшення десорбції водню з гідридної фази MgH_2 МС, синтезованих методом реактивного механічного сплавлення (РМС). Воднева ємність після реактивного подрібнення протягом 20 год. дорівнювала 5,7 % ваг. Внаслідок цього легування зниження термодинамічної стабільності MgH_2 не встановлено. Випробувані матеріали показали високий потенціал як сплавів для зберігання водню, особливо для стаціонарного застосування.

Ключові слова: механічний сплав, воденьсорбційні властивості, термічна стійкість, кінетика.