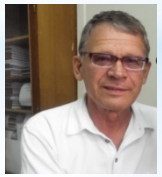
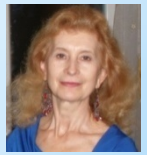
TARGETED COMPREHENSIVE PROGRAM SCIENTIFIC RESEARCH NAS OF UKRAINE

Development of scientific foundations for obtaining, storage and use of hydrogen in autonomous power supply systems

Development of physicochemical principles for the creation of high-capacity hydride-forming materials and their use in stationary hydrogen storage systems and as electrodes for electrochemical energy systems
project № 11-21

Scientific adviser: acad. NASU Solonin Yu.M.
Performers: Ph.D. Ershova O.G., dr. Dobrovolsky V.D.
Frantsevych Institute for Problems of Materials Science, NASU





The purpose of the research of the project was :

To develop high-capacity hydride-forming nanocomposites for applications in stationary hydrogen storage systems Mg with catalytic additives of transition metals Ni and Ti as it has high hydrogen capacity, improved hydrogenation-dehydrogenation kinetics, reduced thermal and increased cyclic stability.

To achieve project goals it was planned to study the influence of synthesis method and conditions for mechanical Mg-based alloys - nanocomposites with alloying additives on their hydrogen sorption properties, hydrogenation/dehydrogenation kinetics, decomposition temperature of the $Mg(Me)H_2$ hydride phases and on stabilizing their nanostructure during subsequent cyclic heating/cooling.

The 2 mechanical-nanocomposite magnesium alloys with an adding of 10% wt. Ni (denoted MA1, MA2) and 2 mechanical-nanocomposite magnesium alloys with adding 10 % wt. Ti (denoted MA4 and MA5) were synthesized using one method of reactive mechanochemical alloying (RMA) but in two different manners.

Mechanical alloy MA1, MA3 was obtained by reactive grinding of Mg powder mixed with Ni, Ti for 20 hours,

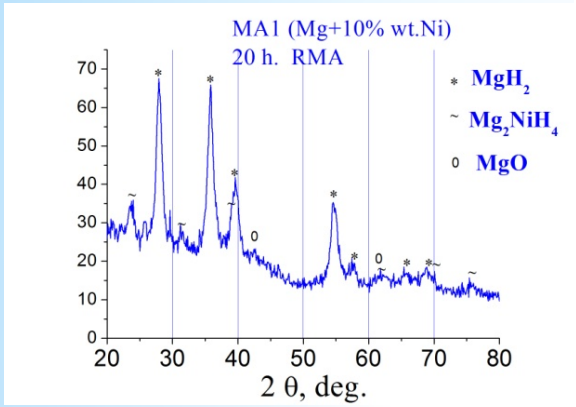
Mechanical alloy MA2, MA4 was obtained by reactive grinding of MgH_2 powder (obtained by hydrogenation of Mg powder from the gas phase on a Sievers type facility) with a Ni, Ti for 20 hours

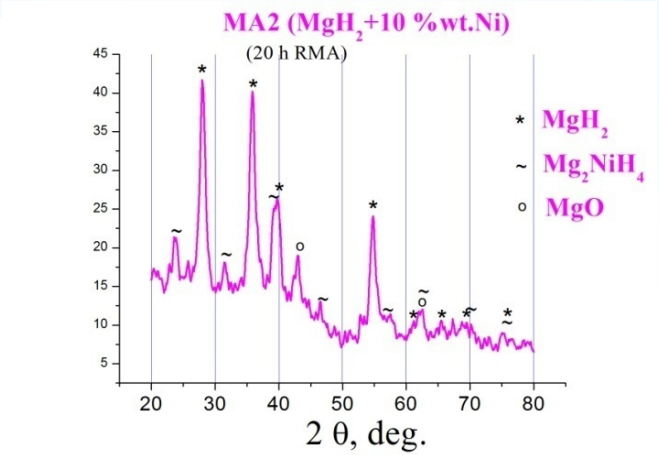
For comparison, under the same conditions of reactive grinding of Mg powder in a hydrogen atmosphere for 20 hours, a MgH_2 hydride phase without Ni (mechanical alloy MA5) was obtained.

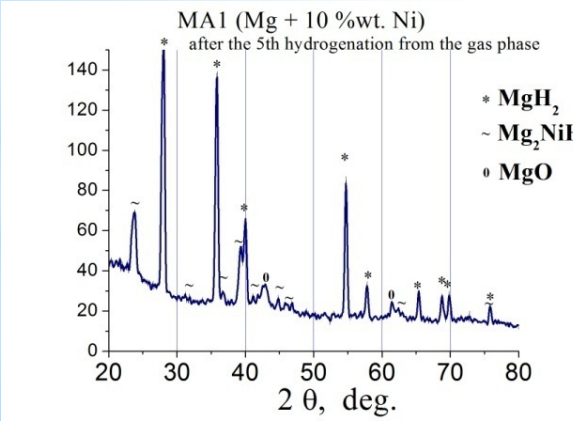
Mechanical alloying by reactive grinding of all powder mixtures was performed in a Retch ball mill with 10 mm steel balls in hydrogen atmosphere at a pressure of 1.2 MPa and a speed of 450 rpm. Direct gas-phase hydrogenation (GPH) from MA1–MA4 materials was performed after being synthesized at a 5.0 MPa hydrogen pressure and 400 ^{0}C in the reactor.

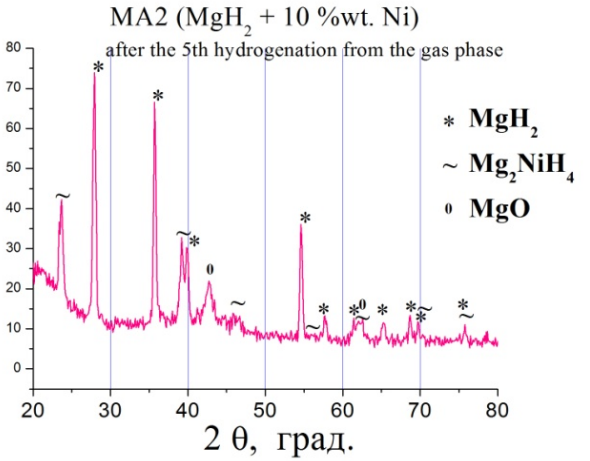
X-ray phase analyze of mechanical alloy-nanocomposites

An automatic computerized DRON-3M diffractometer was employed for the X-ray phase and X-ray structural analysis of the samples. The X-Ray diffraction patterns were obtained using CuKα -radiation with a graphite monochromator. The profiles of diffraction lines were plotted with scanning steps of 0.1⁰ and 15-20 sec exposure at each point of the spectrum.









X-ray phase analysis showed that the mechanical alloys MA1, MA2, MA3, and MA4 synthesized by the RMA method are nanocomposites due to reactive mechanical doping of Ni and Ti.

After the first cycles of hydrogenation/dehydrogenation from the gas phase, all MAs reveal no changes in their phase composition.

X-ray structural analyze of mechanical alloy-nanocomposites

The parameters of the crystal lattice a,c (Å) and the volume V(Å³) of the unit cell for the MgH_2 hydride phase of mechanical alloys-composites (obtained after 20 hours of RMA and the 5 cycles of the gas phase hydrogenation (GPH).

Mechanical alloy-nanocomposites	Phase MgH_2	
	RMA, Å	GPH, Å
MA1 (Mg+10wt.% Ni)	a = 4,5123 c = 3,0345 V= 62,236	a=4,5132 c=3,0170 V=61,453
MA2 (MgH_2+10wt.% Ni)	a = 4,5280 c = 3,0217 V= 61,953	a = 4,5154 c = 3,0209 V= 61,593
MA3 (Mg+10wt.% Ti)	a = 4,4618 c = 3,0411 V= 60,541	a = 4,5089 c = 3,0175 V= 61,346
MA4 (MgH_2+10wt.% Ti)	a = 4,5020 c = 3,0200 V= 61,209	a = 4,5154 c = 3,0224 V= 61,623
MA5 (Mg without Ni i Ti)	a = 4,5232 c = 3,0161 V= 61,707	a = 4,5140 c = 3,0195 V= 61,526

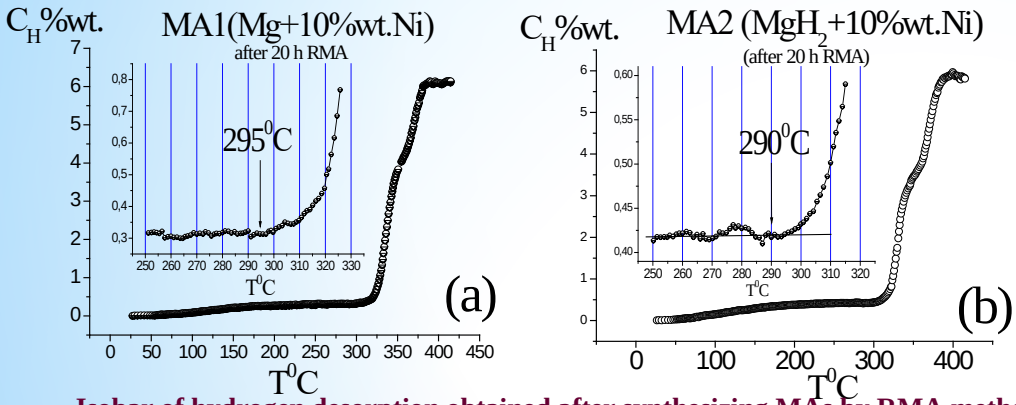
The crystallites (grains) size of the MgH_2 hydride phase in all MAs determined by the approximation method using Selyakov – Scherrer equation $D_{h,k,l} = 0.94\,\lambda / \beta \cos \Theta$

Average particle size and crystallites (grains) size of the MgH_2 hydride phase in all MAs after 20 hours of RMA and the 5 cycles of the gas phase hydrogenation (GPH).

Mechanical alloy-nanocomposites	Crystallite size, nm		$D_{part.}$, µm
	RMA	GPH	RMA
MA1 (Mg+10wt.% Ni)	10.4	22.2	0.27
MA2 (MgH_2+10wt.% Ni)	12,6	29.2	0.32
MA3 (Mg+10wt.% Ti)	8.1	30.5	0.4
MA4 (MgH_2+10wt.% Ti)	11.4	31	0.35
MA5 (Mg without Ni i Ti	12	142	0.69

The thermal behavior of mechanical alloys nano-composite

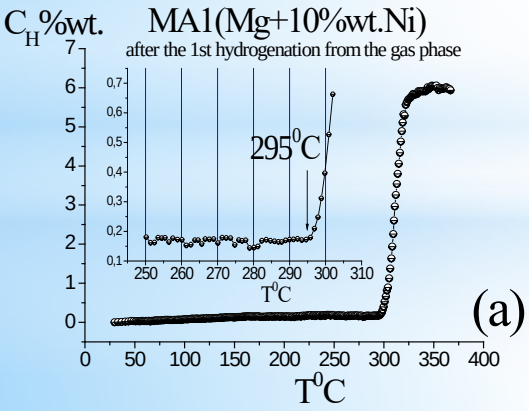
The effect of Ni and Ti doping and the method of obtaining the hydride MgH_2 phase for synthesized MAs on its thermal stability and decomposition temperature was examined through hydrogen desorption from MA1-MA4 by the thermodesorption spectroscopy (TDS) method.

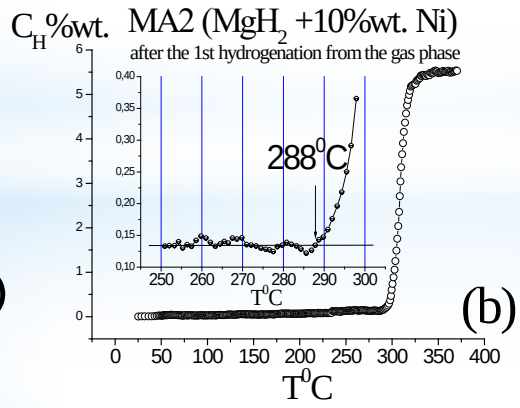


Isobar of hydrogen desorption obtained after synthesizing MAs by RMA method: a- MA1(Mg+ 10 wt.%Ni); b - MA2(MgH_2 +10 wt.% Ni)

Unique possibilities:

TDS is carried out by original apparatus and it allows measuring hydrogen-sorption properties and thermal stabilities of the mechanical alloys using methods of isobaric and isochoric thermal desorption spectroscopy and allows also studying kinetics of processes of hydrogen desorption-resorption from hydride phases of the mechanical alloys. The apparatus allows also measurements of isobars of hydrogen desorption-resorption at hydrogen P = 0.1-1.0 MPa in the reactor, to provide hydrogenation-dehydrogenation of the samples and temperatures 20 °C - 1000 °C.



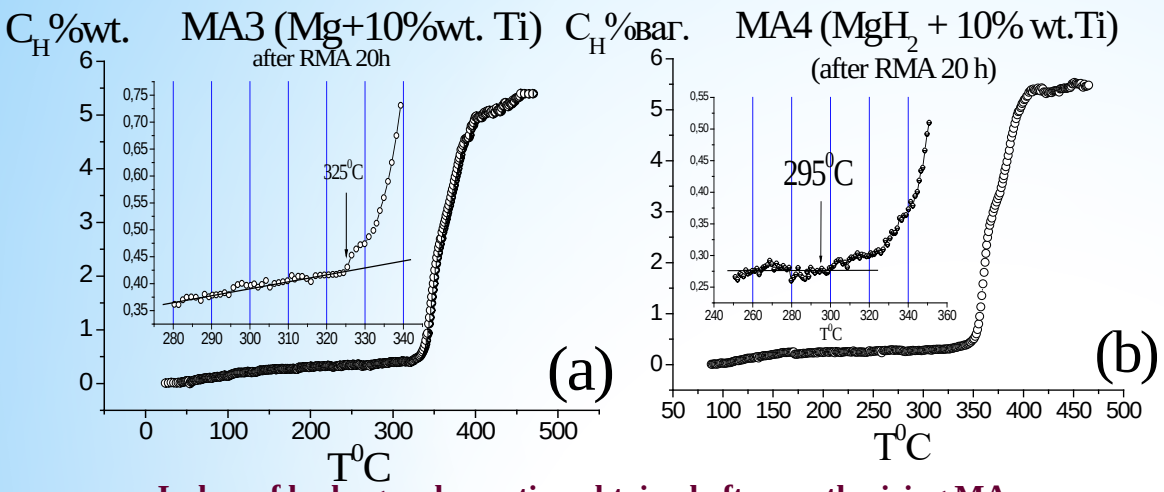


Isobar of hydrogen desorption obtained after the first direct GPH of mechanical alloys: a- MA1(Mg+ 10 wt.%Ni); b - MA2(MgH_2 +10 wt.% Ni)

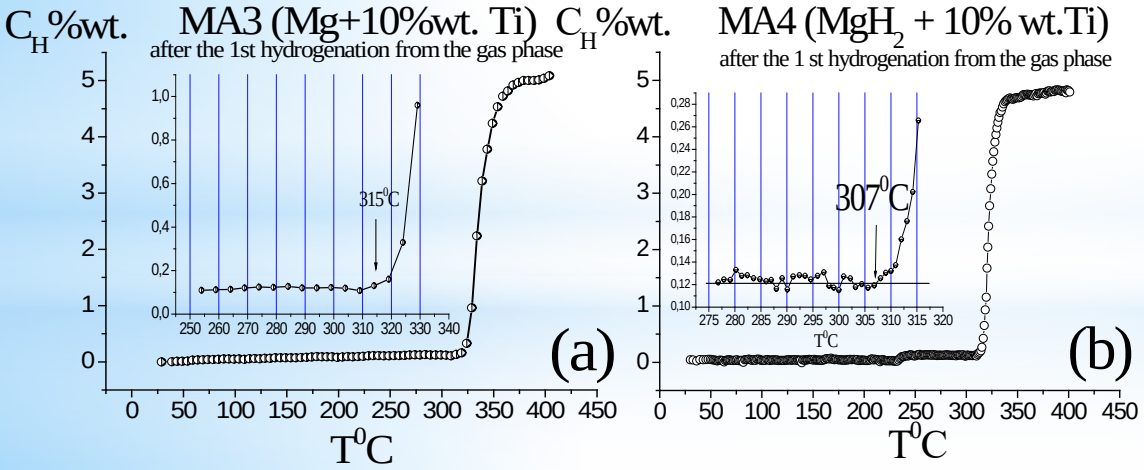
The beginning temperature ($T_{beg.}$) of hydrogen desorption from the MgH_2 hydride phase in MA1-MA5 and its hydrogen capacity

Mechanical alloys-nanjcomposites	RMA		GPH,1-st cycle	
	$T_{beg.}$ ^{0}C	C_{H2}, %wt.	$T_{beg.}$, ^{0}C	C_{H2}, %wt.
MA1 (Mg + 10wt.% Ni)	295	6.1	295	5.94
MA2 (MgH_2 +10wt.%Ni)	290	5.8	288	5.5
MA3 (Mg + 10wt.% Ti)	325	5.4	315	5.3
MA4 (MgH_2+10wt.% Ti)	295	5.5	307	4.9
MA5 (without Ni and Ti)	288	7.4	290	6.3

Hydrogen desorption isobars from all MAs were obtained at a constant hydrogen pressure in the reactor of 0.1MPa and a heating rate of 3 deg./min.



Isobar of hydrogen desorption obtained after synthesizing MAs by RMA method: a-MA3(Mg+10wt.% Ti); b-MA4(MgH_2+10wt.% Ti)



Isobar of hydrogen desorption obtained after the first direct GPH of mechanical alloys: a-MA3(Mg+10wt.% Ti); b-MA4(MgH_2+10wt.% Ti)

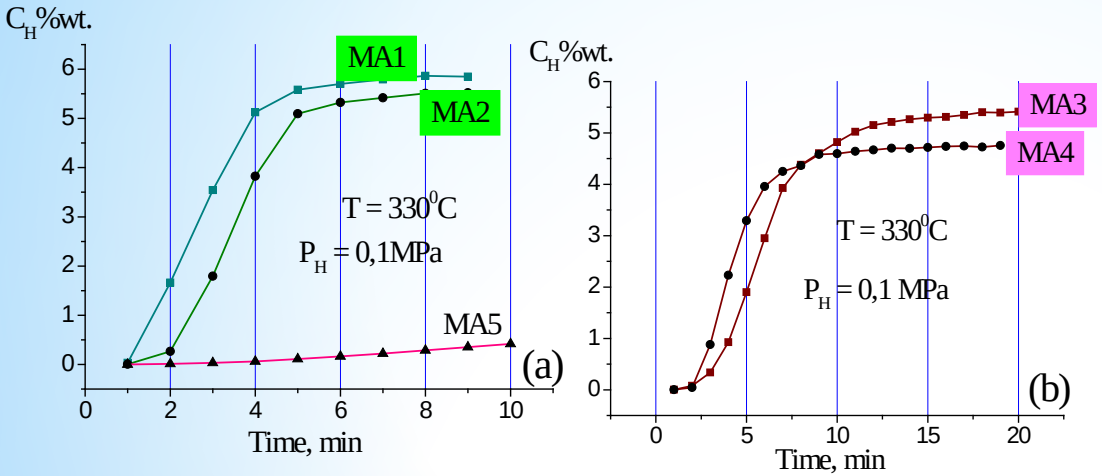
It was found that there are no effects of transition metal additives and method of obtaining MAs on the beginning temperature of hydrogen desorption and corresponding beginning temperature of their MgH_2 hydride phase decomposition for all MAs.

The thermodynamic stability of the MgH_2 phase did not decrease since within the chosen method of obtaining MAs (and, consequently, their main MgH_2 hydride phase), no solid solutions of Ti or Ni in magnesium were formed, hydrides of which, according to theoretical forecasts, should have a lower enthalpy of formation than the enthalpy of formation of MgH_2.

Experimental confirmation of the above can be found in the composition of MC1, MC2 phase Mg2NiH4 and in the composition of MC3, MC4 phase TiH2, the formation of which took a large amount of metallic Ni and Ti.

Kinetics of the hydrogen desorption from mechanical alloys-nanocomposites

The kinetics of hydrogen desorption from the MgH_2 hydride phase in all synthesized MAs after their GPH under the same conditions has been investigated at temperatures of 310 and 330 °C and a constant hydrogen pressure in the reactor of 0,1 MPa



The effect of improving the kinetics by adding Ni to magnesium is much more significant than in the case of Ti. It is evidenced by the experimentally recorded 16-fold and 11-fold reduction of the total desorbed hydrogen release time for MA1 and MA2, respectively, at a constant temperature of 330 ^{0}C and the constant pressure of 0.1 MPa. For MA3 and MA4, the release time decreased by 5.7 and 6.2 times, respectively, compared with the time of releasing of all hydrogen in the case of MA5.

Kinetic curves of H_2 desorption from: a - MA1(Mg+ 10 wt.%Ni), MA2(MgH_2 +10 wt.% Ni) MA5(Mg without Ni,Ti) ; b - MA3 (Mg + 10 wt.%Ti), MA4 (MgH_2 + 10 wt.%Ti)

Desorption time (min) of half ($\tau_{1/2}$) and total (τ_f) hydrogen amount from MgH_2 hydride phase in all MAs

Mechanical alloy - nanocomposites	310 ^{0}C		330 ^{0}C	
	$\tau_{1/2}$	τ_f	$\tau_{1/2}$	τ_f
MA1 (Mg+ 10 wt.%Ni)	2,2	7	1.6	5
MA2 (MgH_2 +10 wt.% Ni)	3,4	11	2.5	7
MA3 (Mg + 10 wt.%Ti)	8,5	25	4.7	14
MA4 (MgH_2 + 10 wt.%Ti)	5,2	14	3.1	13
MA5 (Mg without Ni,Ti)	55	160	30	80

Given result our and other research (G.Liang; N.Hanada; L.Xie) it is logical to assume that when adding 10 wt % Ni or 10 wt % Ti the above 16-fold and 6-fold reduction in the release time of all amount of hydrogen from MA1 (Mg + 10% wt. Ni and MA4 (MgH_2 + 10 wt.%Ti), compared to MA5, is mainly due to a decrease in the activation energy of hydrogen desorption from MgH_2

The study the influence of synthesis method and conditions for mechanical Mg-based alloys - nanocomposites with alloying additives

on their hydrogen sorption properties, hydrogenation/dehydrogenation kinetics, decomposition temperature of the Mg(Me)H_2 hydride phases and on stabilizing their nanostructure during subsequent cyclic heating/cooling

It can be stated that of the two methods used to obtain MC1 and MC2, their best kinetic characteristics are provided by the method of obtaining by reactive grinding of a mixture of powders Mg +10% by wt. Ni (and not powders MgH2 +10% wt. Ni).

How can this fact be explained?

● The faster kinetics of hydrogen desorption from the MgH2 hydride phase of MC1 (Mg + 10 wt.% Ni) may be due to the smaller size of its crystallites (grains) and, accordingly, the shorter length of diffusion paths for hydrogen atoms than in the MgH2 hydride phase of MC2 (MgH2 + 10 wt.% Ni).

● As a result of 5 cycles of heating / cooling of samples MC1, MC2 during their hydrogenation from the gas phase there is an increase in the grain size of the hydride phase MgH2 of the above mechanical alloys-nanocomposites, respectively, from 10.4 to 22.2 nm (ie 2.13 times) and from 12.6 to 29.2 nm (ie 2.32 times). In the case of a mechanical alloy without Ni in the same conditions of cyclic heating / cooling, the growth of grains of the hydride phase of MgH2 is 12 times.

● By preventing the grain sizes of the MgH2 hydride phase from growing, Ni ensures, very importantly, the stability of its nanostructure during cyclic operation, and thus the stability of its operating kinetic and hydrogen sorption characteristics. Thus, **Ni** as an additive to magnesium in the synthesis process acts **as a dispersant,** and subsequently, in the process of cyclic operation of these MA (during operation) acts **as a stabilizer** of their nanostructure, inhibiting the growth of grain size of the hydride phase MgH2.

CONCLUSION

■ **Four mechanical alloys-nanocomposites based on magnesium with the addition of 10 % wt.Ni (MA1, MA2) and 10% wt.Ti (MA3, MA4) were synthesized by one method of reactive mechanical alloying (RMA) but in different manners. The hydrogen capacity, thermal stability, and kinetics of hydrogen desorption from the MgH_2 hydride phase of the obtained MAs were studied using thermodesorption spectroscopy at a constant hydrogen pressure of 0.1MPa.**

■ **It has been established that the time needed for the total hydrogen release from MA1, MA2, MA3, and MA4 was 5, 7, 14, and 13 minutes, respectively, at a constant hydrogen pressure of 0.1MPa and a temperature of 330 ^{0}C.**

■ **The method of obtaining a mechanical alloy-nanocomposite by reactive grinding of an Mg +10 % wt. Ni rather than MgH_2 +10 % wt. Ni powder mixture has been shown to improve the kinetic characteristics. Faster kinetics of hydrogen desorption from the MgH_2 hydride phase of MA1 (Mg + 10 wt.% Ni) was due to the smaller grain size than the grain size of the MgH_2 hydride phase in MA2 (MgH_2 + 10 wt.% Ni). The effect of obtaining MA3, MA4 with Ti additives on the kinetics of hydrogen desorption from them is different and not noticeable compared to MA1, MA2 with Ni additive.**

■ **The role of the alloying element Ni in improving the kinetics of the process of desorption of hydrogen from MAs obtained in different manners, as well as in stabilizing their nanostructure during cyclic operation by preventing (inhibiting) the growth of the crystallite (grain) of their hydride phase MgH_2, has been elucidated.**

■ **Ascertained the practical absence of the influence of Ni, Ti additives and the manner of MAs production on the temperature of the beginning of hydrogen desorption and the associated temperature of the beginning of decomposition of the hydride phase MgH_2 of MA1 - MA4.**

Possible area of applications

In high-power modules of energy converters, hydride heat pumps, and laboratory installations to research thermal hydrogen desorption features.

Comparative analysis of the study findings

As part of the project devoted to developing methods of deriving and improving the properties of hydrogen-sorption materials for hydrogen storage using Mg-based alloys, we planned to perform research aimed at ***achieving complex characteristics of these materials necessary for their practical application in hydrogen storage facilities***. First and foremost, these characteristics include faster kinetics and lower temperature of full hydrogen release at a pressure of 0.1MPa. To achieve the specified improving performance of the obtained materials, new synthesis methods (mechanical and reactive mechanical alloying) were planned to be applied, also involving mechanical alloying and dispersion processes. That allowed modifying and generating the required hydrogen-sorption properties of alloys, chemical condition of their surfaces by affecting electronic and thermodynamic properties. The role of the method and production conditions, size factor in lowering temperatures and improving the kinetics of the MgH_2 hydride phase decomposition in mechanical alloys-nanocomposites based on magnesium with Ni and Ti transition metals was examined. The optimal composition of alloys and their synthesis conditions providing an improved complex of performance characteristics was determined.

Advantages

The most researchers determine the time of release of hydrogen from the MgH_2 hydride phase in obtained mechanical alloys from the kinetic curves of hydrogen desorption using a volumetric Sieverts-type apparatus rather than those obtained at a constant hydrogen pressure in the reactor 0.1MPa. This fact specified the relevance of this project. Therefore, this work is beneficial since the kinetics of the hydrogen desorption from the synthesized mechanical alloys-composites was studied at constant temperature and constant hydrogen pressure in the reactor 0.1MPa, as required by practice. ***We preferred the isobaric-isothermal method of obtaining kinetic curves over the isochoric-isothermal one used today by most researchers*** on MA (Mg + 10% wt. Ni) (Song M.Y. (1995) and MA (MgH_2 + 10% wt. Ni) (Yahya M.S.(2018)). It allowed studying the role of Ni and Ti alloying elements and the manners of obtaining MAs to improve kinetics and reduce the decomposition temperature of the MgH_2 hydride phase in synthesized MAs in more detail.

Competitors

Department for Mater.Sci.&Engineer., Zhejiang University, China
Department for Mater.Univer London, UK
Course in Materials Science &Chemistry, Tokai University, Numazu, Japan
Institute for Energy Technology, P.O. Box 40, N-2027 Kjeller, Norway.
Helmholtz-Zentrum Gentre for Materials and Coastal Research, Germany

Technology Readiness Level

Based on the authors' research in the last 10 years on the role of a small additives (10% wt.) separately for each of the alloying elements Ti, Ni in reducing thermal stability and improving the decomposition kinetics of stoichiometric MgH_2 hydride, the technology for obtaining high-capacity hydrogen-absorbing magnesium-based materials with complex characteristics was developed, ensuring the practical use of these materials in stationary hydrogen storage systems. At present, the synthesis modes and characteristics of the developed mechanical alloys-nanocomposites for hydrogen storage determined on laboratory equipment require further adjustment and verification on mechanical alloys obtained in industrial production conditions.

PUBLICATION

O.G. Ershova, V.D. Dobrovolsky, Yu.M. Solonin, A.Yu.Koval Hydrogen sorption properties, thermal stability, and kinetics of hydrogen desorption from the hydride phase of the MgH_2 of a mechanical alloy of magnesium with Ti and Y, *Met.Phys. and Adv.l Tech.* , 2019, vol.41, pp.981-1001.

O.G. Ershova, V.D. Dobrovolsky, Yu.M. Solonin. Kinetics of hydrogen desorption, hydrogen-sorption properties, thermal stability of mechanical alloy of magnesium with Ti and REM. XX ANNIVERSARY INTERNATIONAL SCIENTIFIC-PRACTICAL CONFERENCE "RENEWABLE ENERGY AND ENERGY EFFICIENCY IN THE XXI CENTURY". - Kyiv. - K .: Interservice,2019, p. 396-399.

O. G. Ershova, Dobrovolsky V.D., Solonin Yu.M. The Influence of Complex Doping on Kinetics of Decomposition and Thermal Stability of Mg-Based Mechanical Alloys. Physics and Chemistry of solid state 2019; 20(4): 406-15 (doi:10.15330/pcss.20.4.406-415).

O. G. Ershova, Dobrovolsky V.D., Solonin Yu.M. The influence of the alloying addition Ti, Fe, Ni on hydrogen sorption properties, temperature and kinetics of decomposition of the MgH2 hydride phase of mechanical alloys - composites. XX1 ANNIVERSARY INTERNATIONAL SCIENTIFIC-PRACTICAL CONFERENCE "RENEWABLE ENERGY AND ENERGY EFFICIENCY IN THE XXI CENTURY". - Kyiv. – K.: Interservice, 2020 , p. 243-247

O.G. Ershova, V.D. Dobrovolsky, Yu.M. Solonin. Hydrogen Sorption Properties, Thermal Stability and Kinetics of Hydrogen Desorption From the Hydride Phase of The MgH2 of a Mechanical Alloys of Magnesium with Ti, Ni and Y. *Physics and chemistry of solid state*; 2020, vol. 21,pp.167-175.

O.G. Ershova, V.D. Dobrovolsky, Yu.M. Solonin.The effect of transition metals and Y additives on decomposition kinetics and thermal stability of the MgH_2 hydride phase of mechanical alloy-composites. *International Independent Scientific Journal*, 2020, vol.1, No. 20,pp. 35-45.

O.G. Ershova, V.D. Dobrovolsky, Y.M. Solonin. Development of physicochemical principles for the creation of high-capacity hydride-forming materials and their use in stationary hydrogen storage systems and as electrodes for electrochemical energy systems, Monograph «Development of scientific bases for hydrogen production, storage and use in autonomous energy supply». 2021

Інститут проблем матеріалознавства ім. І.М. Францевича НАН України

Дякуємо за увагу

Frantsevych Institute for Problems of Materials Science, NASU, 3 Krzhyzhanovsky str., 03142 Kyiv, Ukraine

Thank you for attention