



**Institute of Solid State Chemistry and Mechanochemistry,
Siberian Branch of RAS
Russia**



**Institut de Chimie de la Matière Condensée de Bordeaux
ICMCB-CNRS, Université Bordeaux 1
France**

MECHANOCHEMICALLY SYNTHESIZED MAGNESIUM- BASED MATERIALS FOR HYDROGEN STORAGE

I.G. Konstanchuk, K.B. Gerasimov, N.Z. Lyakhov, J.-L. Bobet

Main problems of magnesium as hydrogen storage material

◆ **MgH₂ is relatively stable ($\Delta H = -75$ kJ/mol). The equilibrium hydrogen pressure of 0.1MPa is achieved at temperature ~ 550 K**

◆ **Conventional magnesium needs long activation**

◆ **The kinetics of hydrogen absorption by magnesium and decomposition of MgH₂ are not sufficiently fast.**

◆ **The theoretical hydrogen capacity practically is never achieved**

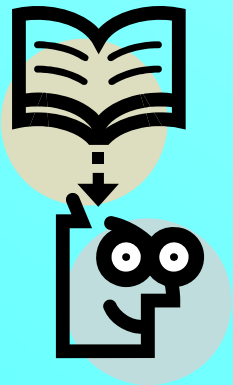
APPROACHES TO IMPROVE HYDRIDING CHARACTERISTICS

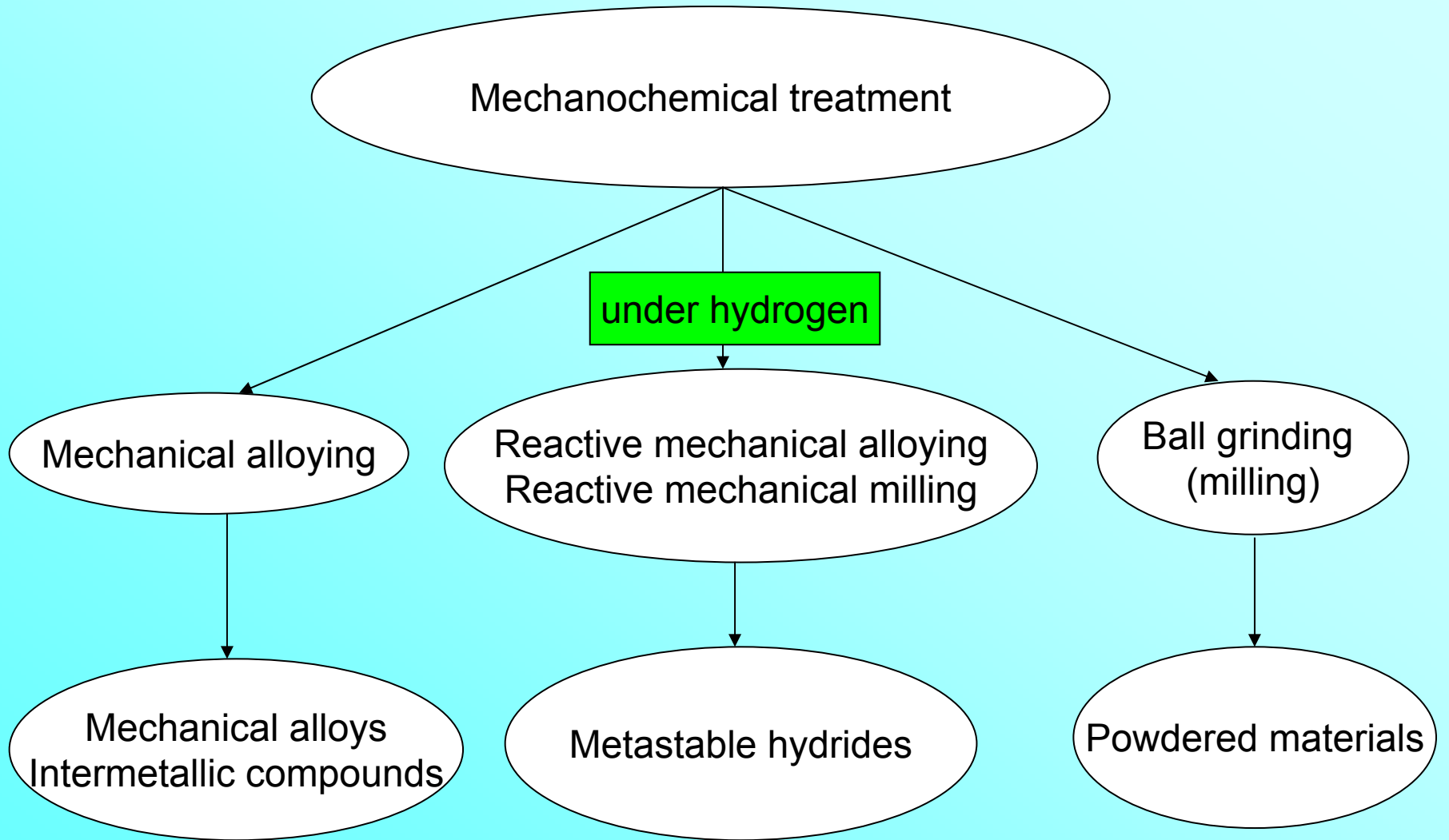
Improving the hydrogen storage properties of known hydrogen absorbing materials
(kinetic aspect)

Modification of thermodynamic parameters of the metal hydrogen system to bring about the P-T-C diagrams to desirable values
(thermodynamic aspect)

Searching for new hydrogen absorbing materials with good hydriding properties

Problem: immiscibility of magnesium with a large number of elements of the Periodic System.





Mechanochemical treatment

under hydrogen

Mechanical alloying

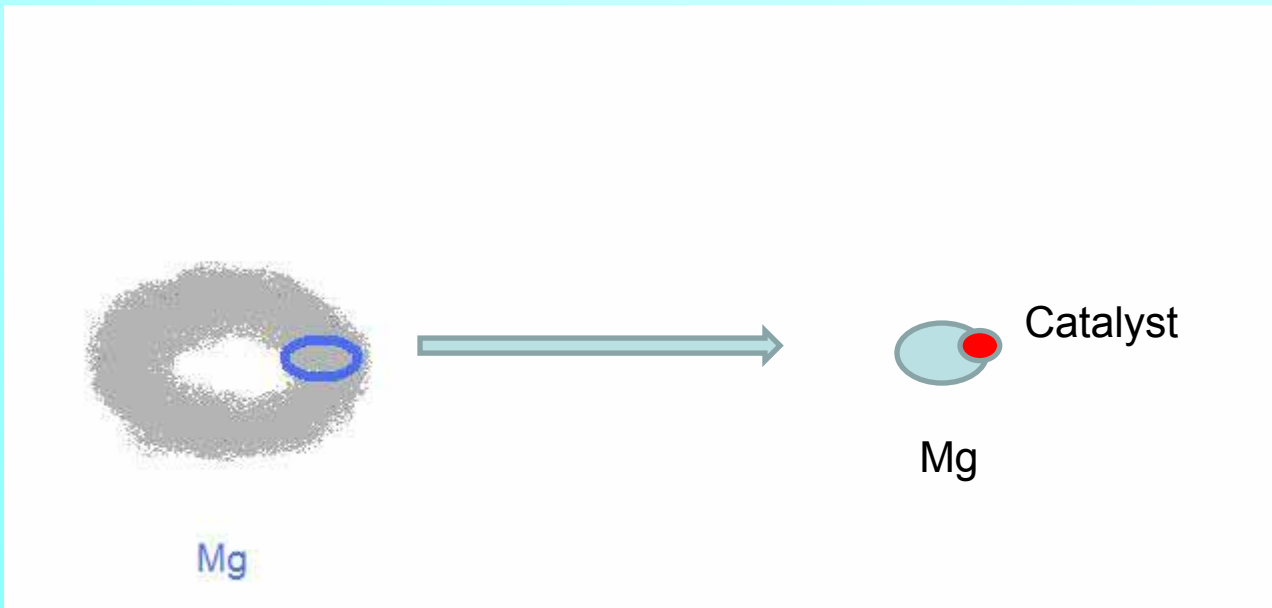
Reactive mechanical alloying
Reactive mechanical milling

Ball grinding
(milling)

Mechanical alloys
Intermetallic compounds

Metastable hydrides

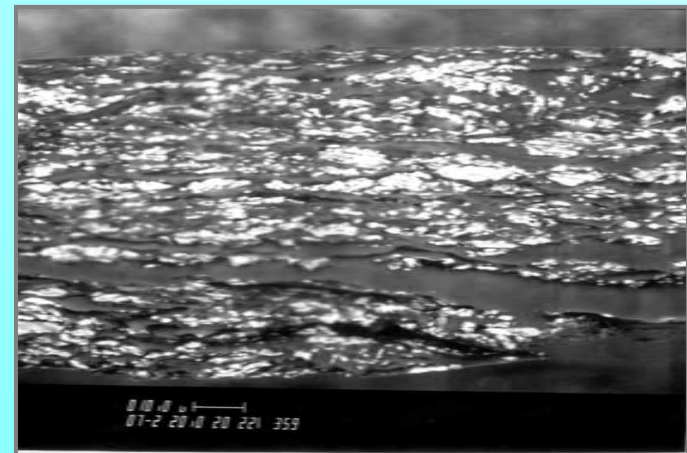
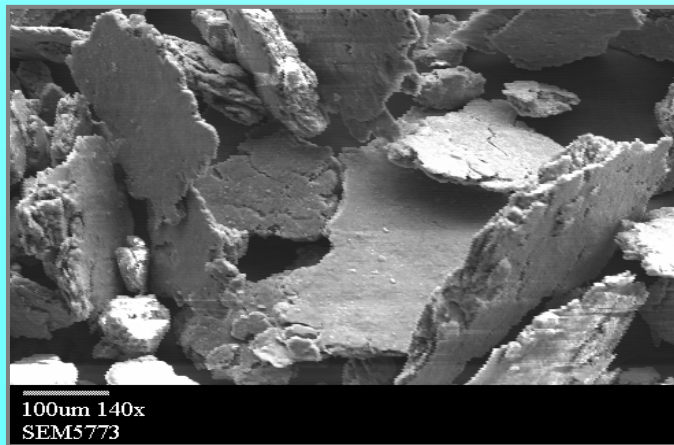
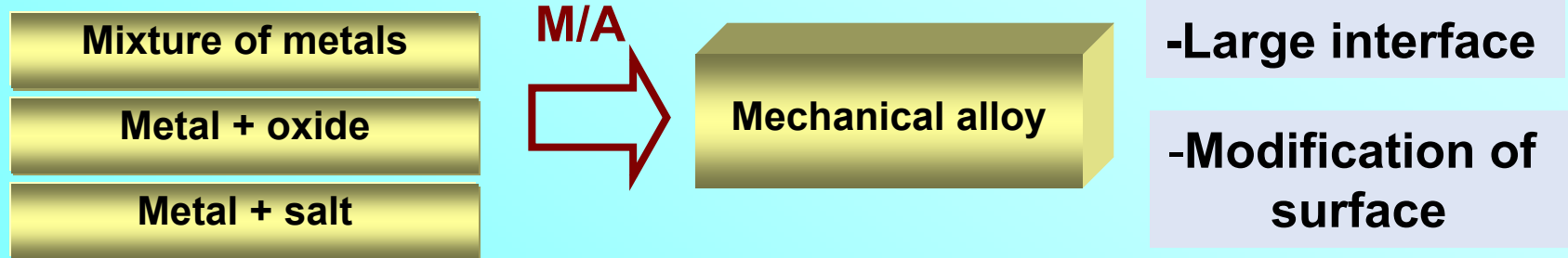
Powdered materials



Addition of catalyst accelerates the hydride formation but decreases the hydrogen capacity not only because of additional weight of the catalyst phase but also due to the earlier formation of a hydride layer.

A possible way to overcome this problem may be found by decreasing the particle size of magnesium and modifying their surface with catalytic additives and/or other chemical reagents which can change the nucleation conditions of the magnesium hydride, the morphology of the hydride layer and the hydrogen permeation through it. Some interparticle layer preventing sintering is also desirable.

Mechanical alloying



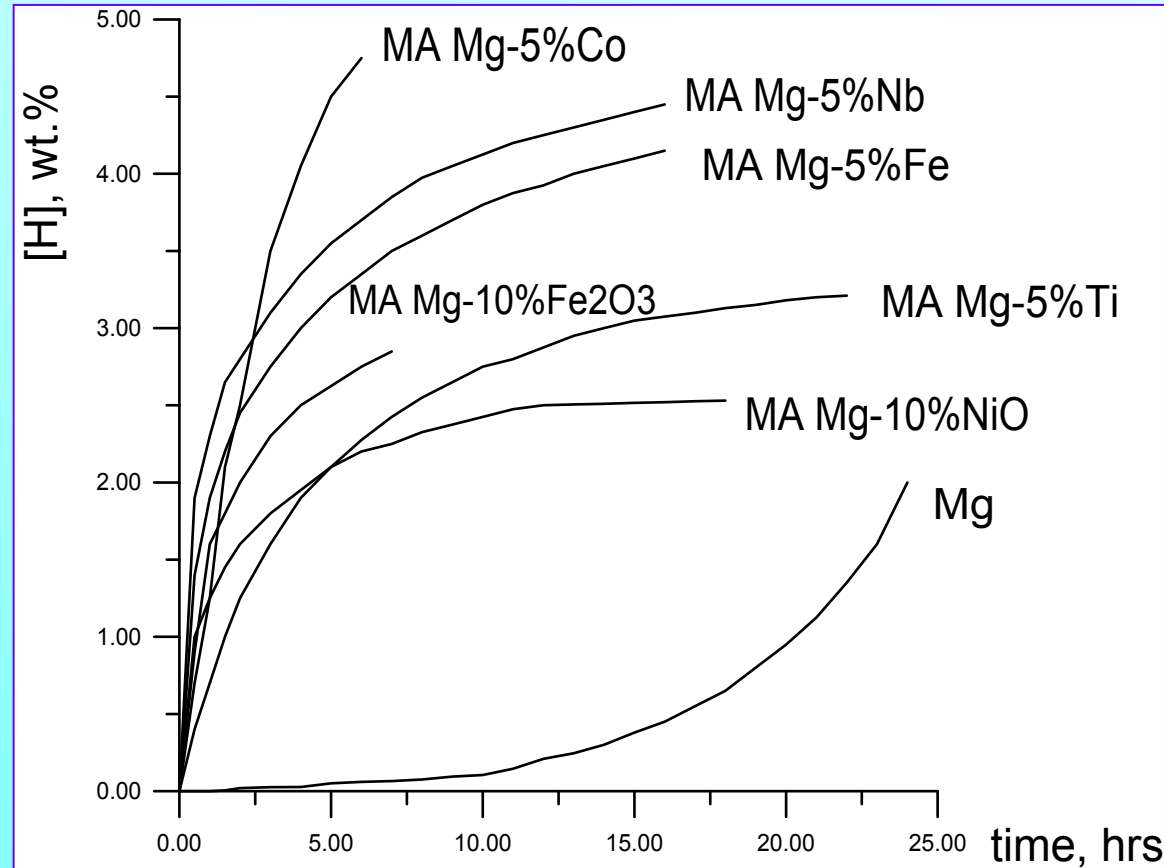
Appearance and microstructure of mechanical alloys (Mg-Ni)

Mechanical alloying

Easy activation

The first hydriding of mechanical alloys starts at maximal rate without any induction period. This sufficiently facilitates the activation process.

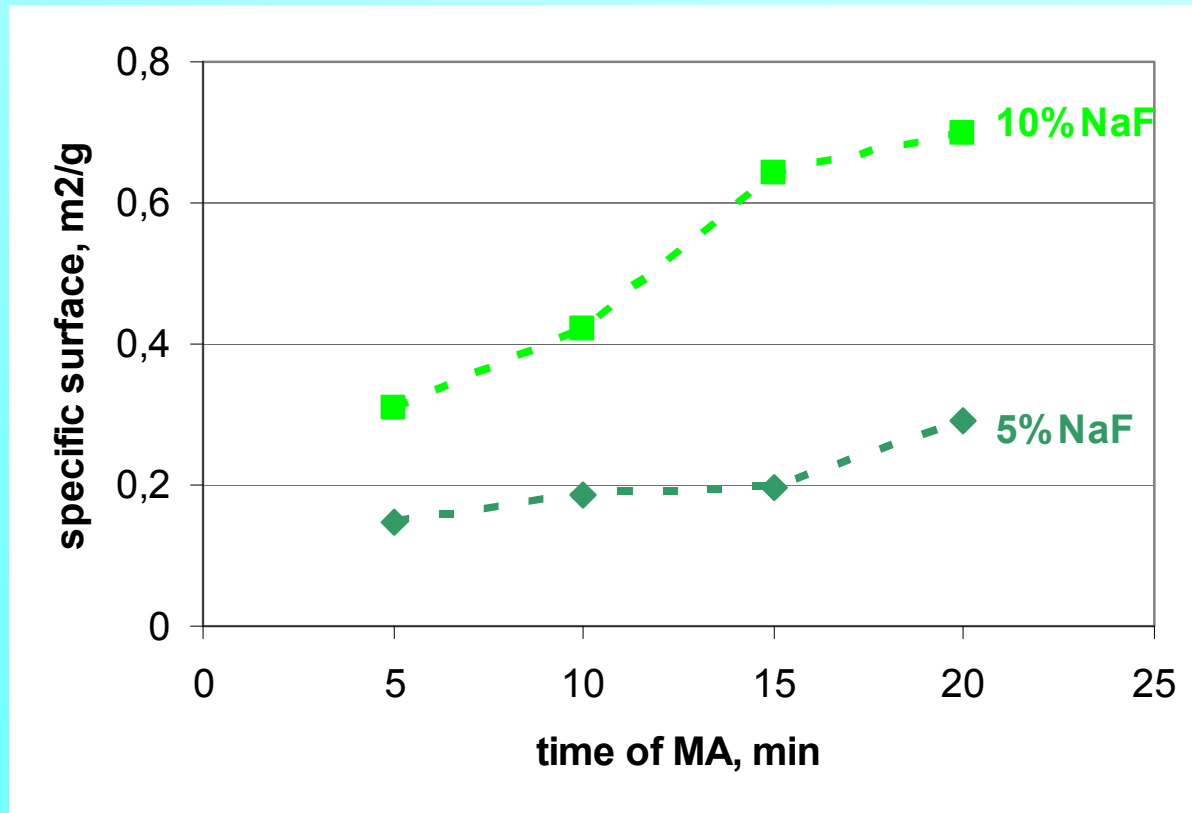
The specific structure of mechanical alloy surface makes catalytic additives accessible to hydrogen, but it is proof against oxygen.



First hydriding of mechanical alloys with various additives,
T=623 K, PH₂= 1.5 MPa

Mechanical alloying

Surface-active additives to magnesium (such as graphite or organic compounds) promote pulverization of metal and increasing hydrogen capacity.

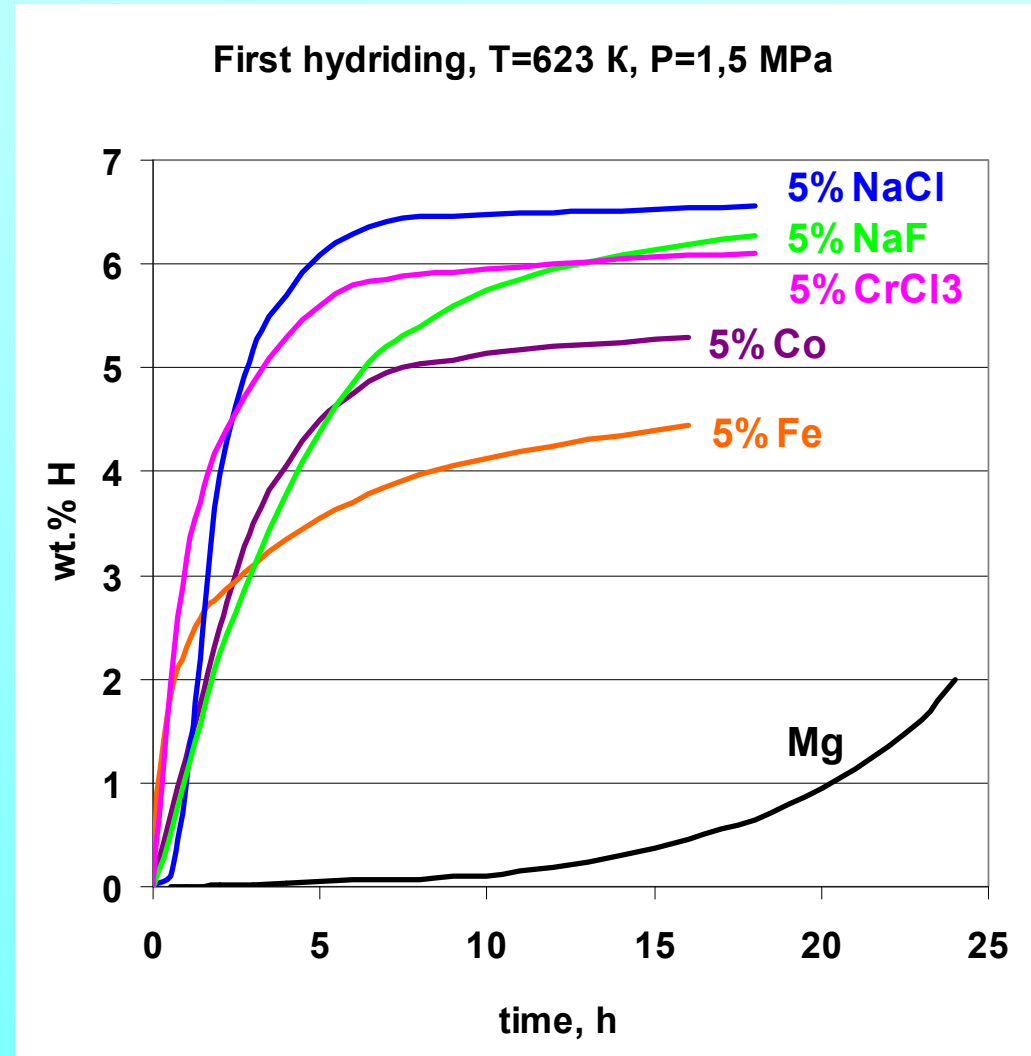


The comminution of the material and modification of its surface take place simultaneously in the course of the mechanical alloying with salt addition.

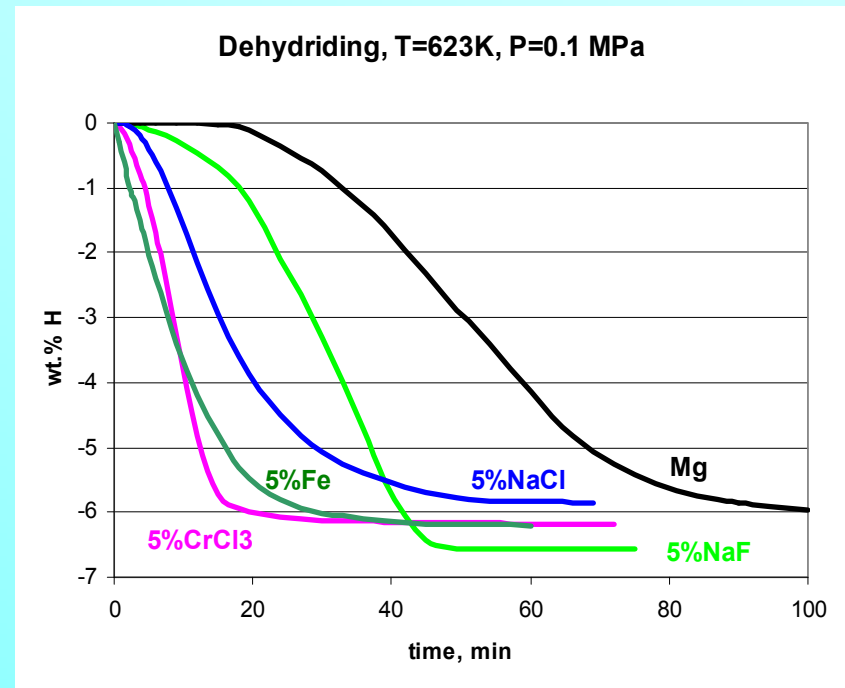
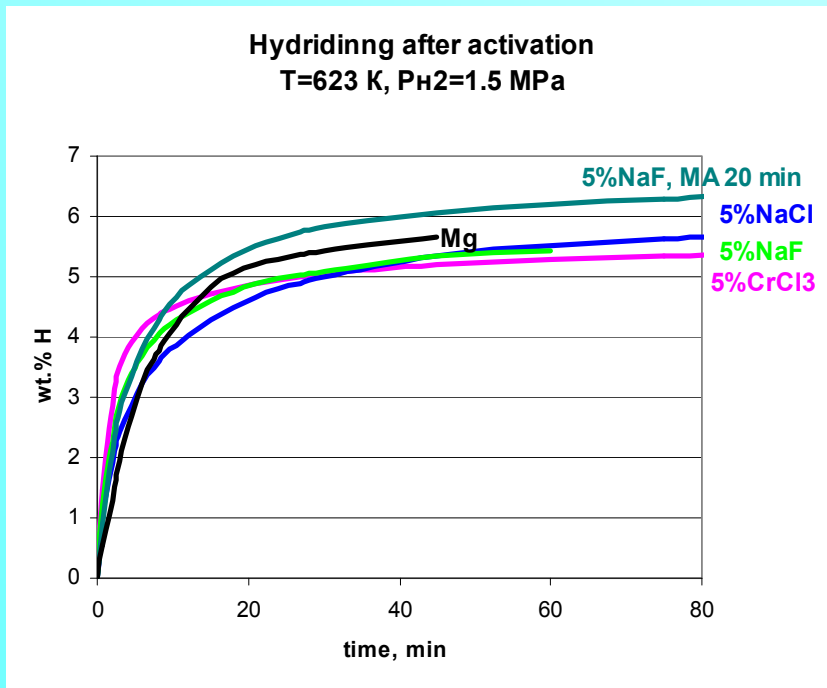
Mechanical alloying

More dispersed Mg-salt mechanical alloys have higher hydrogen capacity than Mg-metal mechanical alloys

It is possible to operate with samples in air without any precautions.



Mechanical alloying

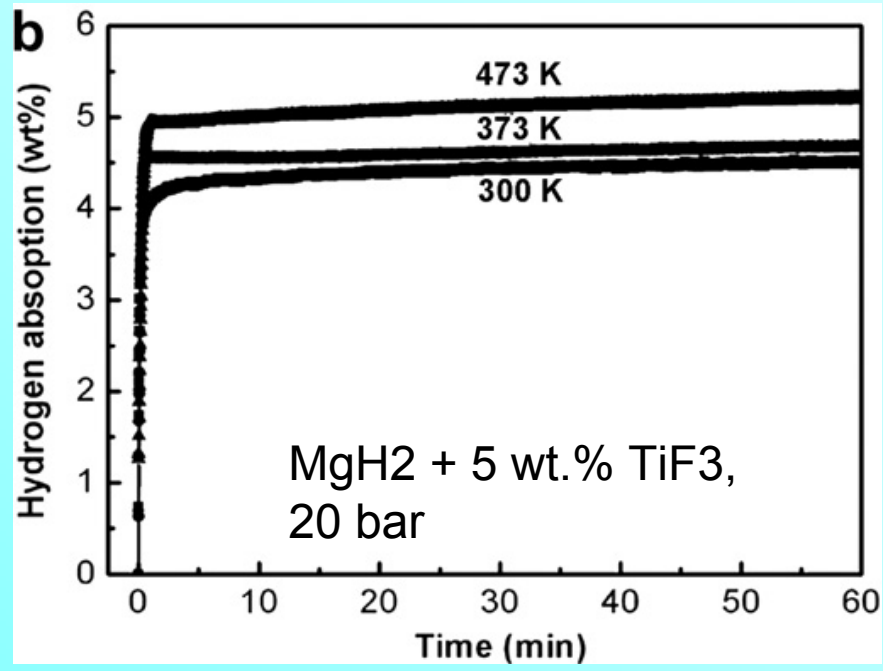
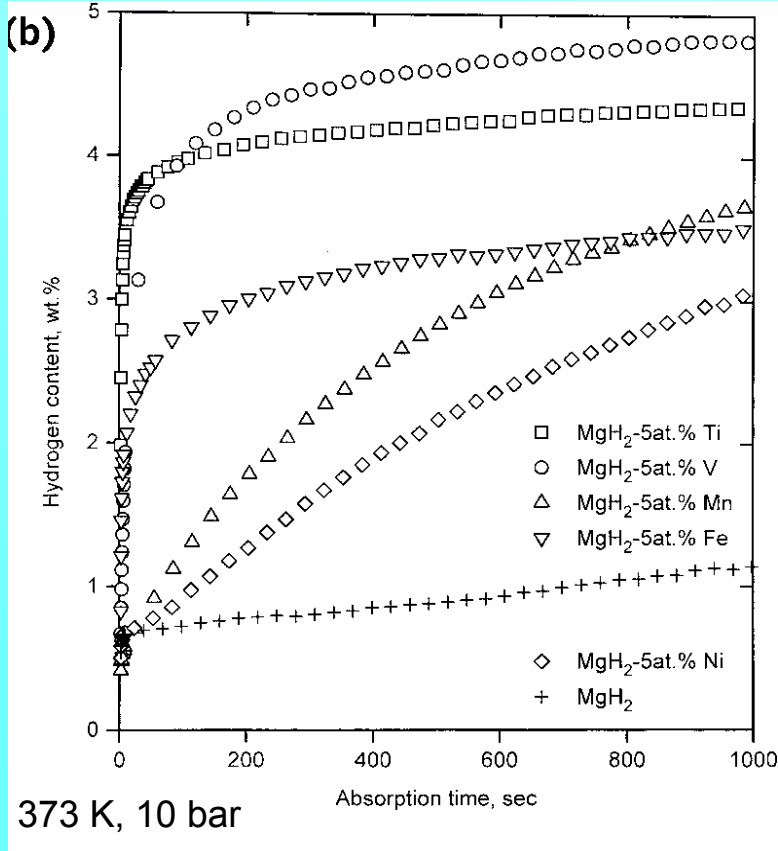


The rates of hydriding and dehydriding at subsequent cycles depend on the nature of additive but always exceed reaction rate of pure magnesium.

kinetic aspect

In recent years the main tendency in improving hydriding properties of magnesium consist in fabrication of **nanocrystalline magnesium-catalyst composites**. As a rule, it significantly accelerates hydriding and dehydriding rates. The main method used for this purpose is **reactive mechanical alloying**.

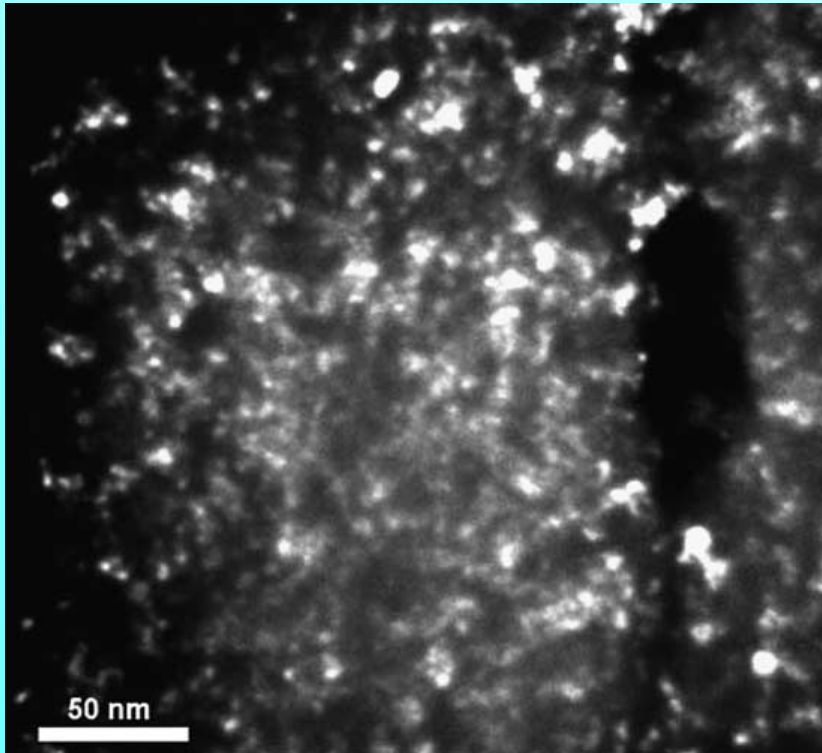
For example



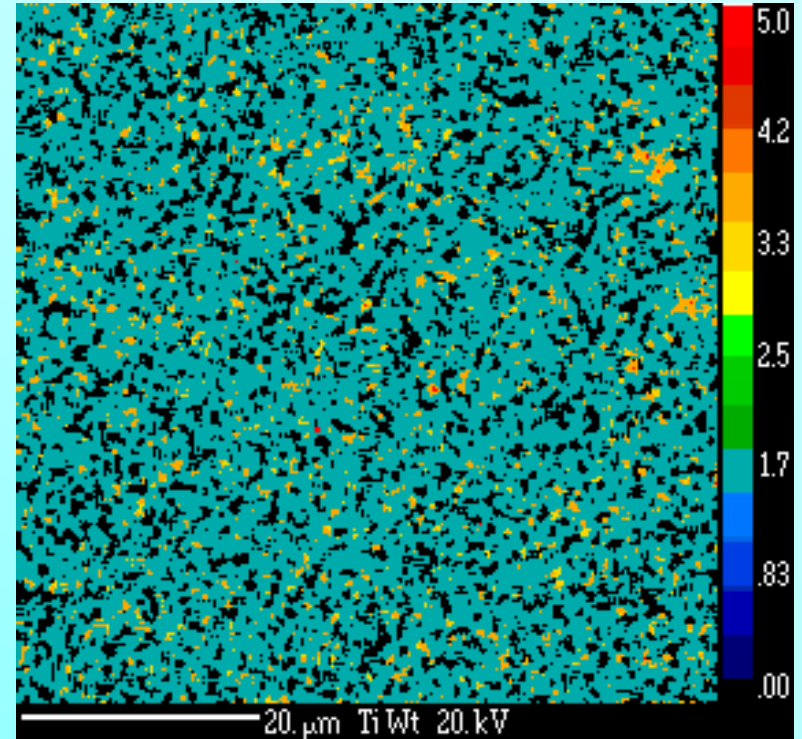
L. Xie et al. Acta Materialia 55 (2007) 4585

G.Liang et al, J. Alloys Compd 292 (1999) 247

Reactive mechanical alloying

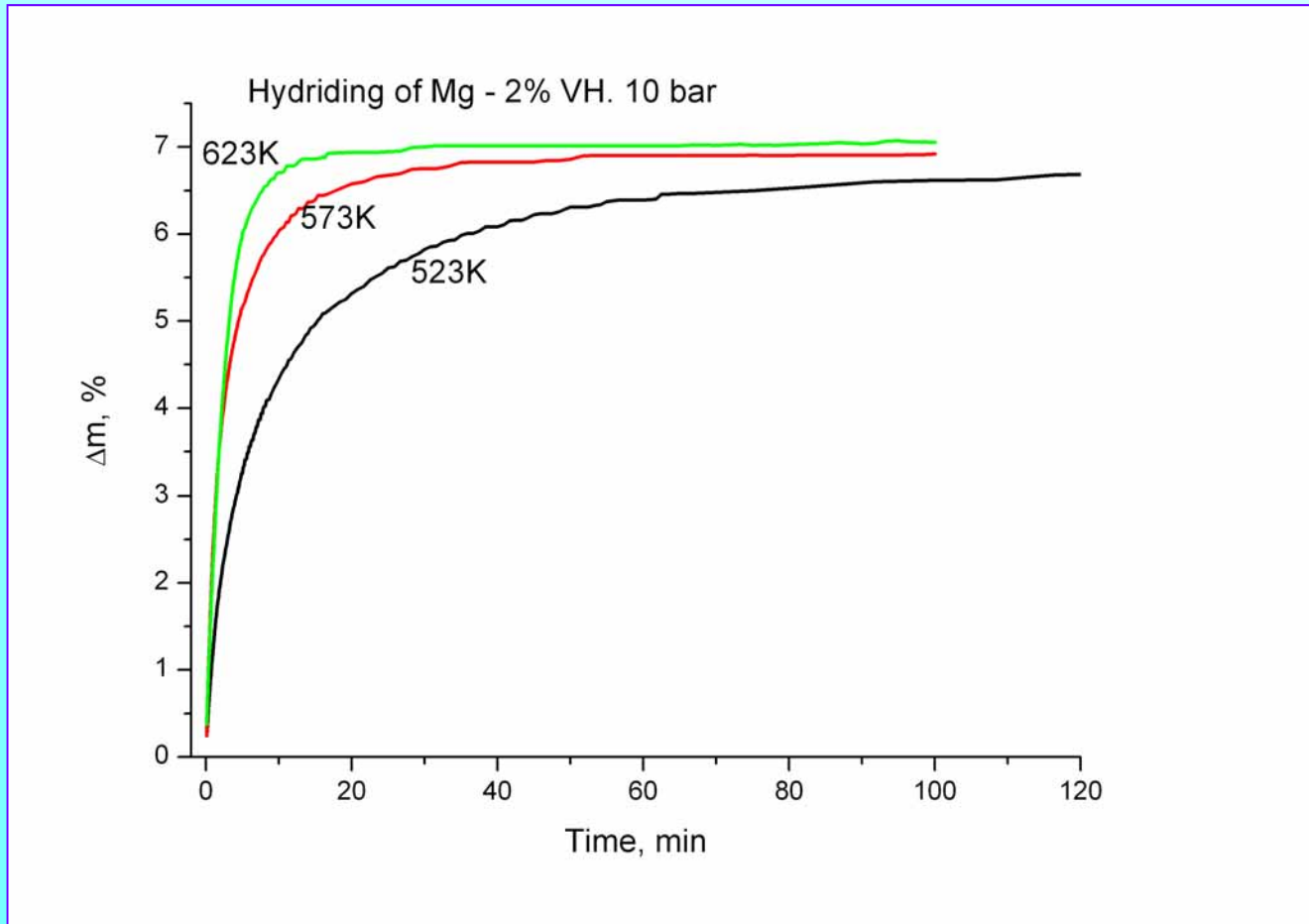


TEM image of nanostructural composite $\text{MgH}_2 + 3\% \text{FeF}_3$ formed in the result of mechanical alloying. (A.R. Yavari et al. *Scripta Materialia*, 52 (2005) 719).



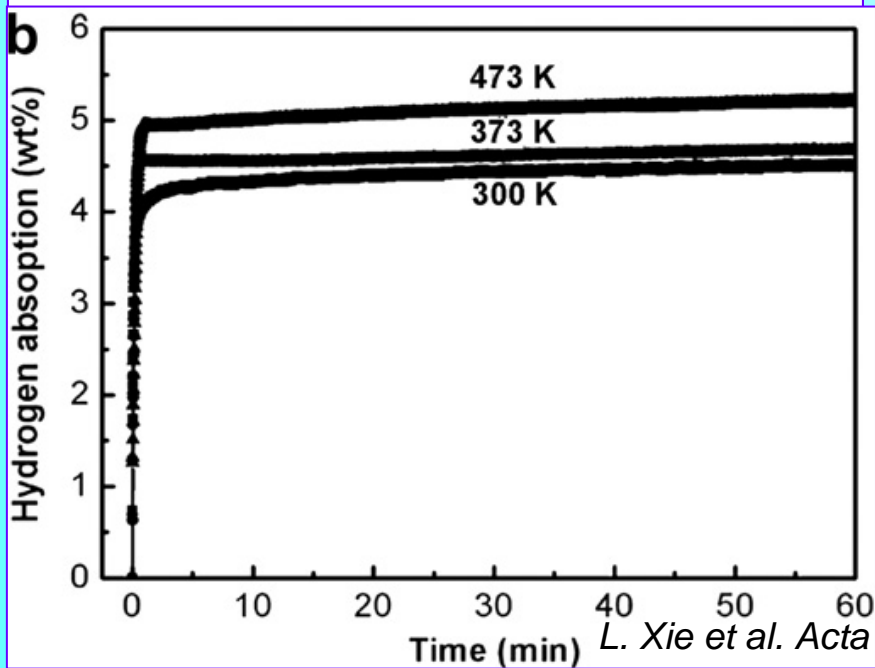
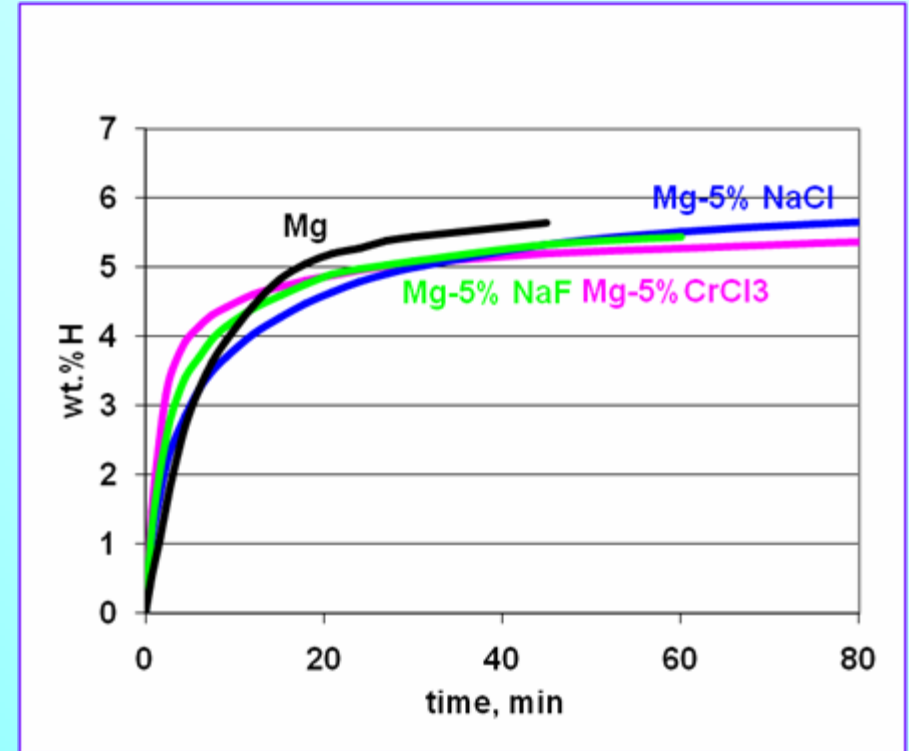
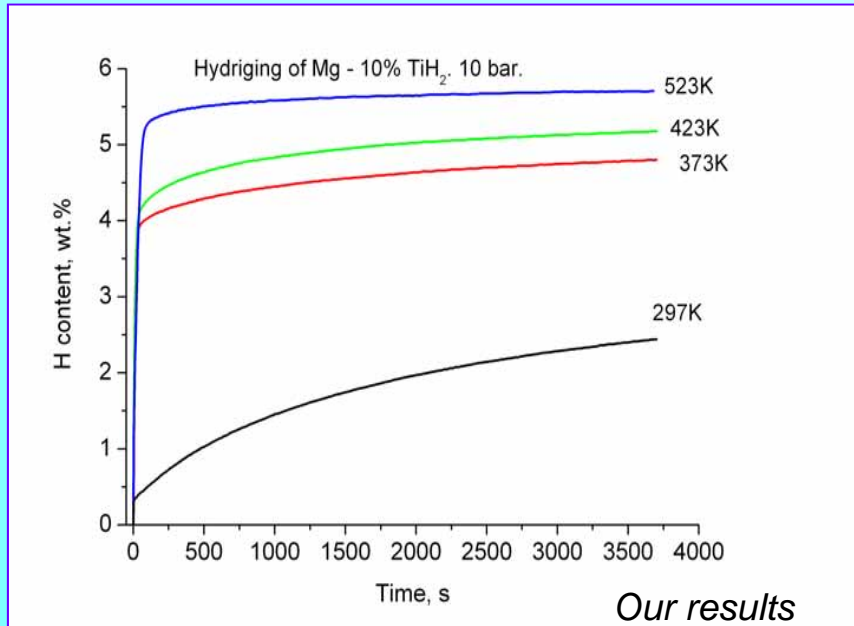
Electron microprobe analysis Mg-2wt%Ti-3wt%NaF mechanically alloyed under hydrogen atmosphere

Reactive mechanical alloying



It is possible to achieve hydrogen capacity higher than **4 wt% at 373 K** and close to **7 wt.% at 623 K** in nanostructural composites obtained in the result of reactive mechanical alloying of Mg or MgH₂ with the addition of **Ti, V** or **Nb**.

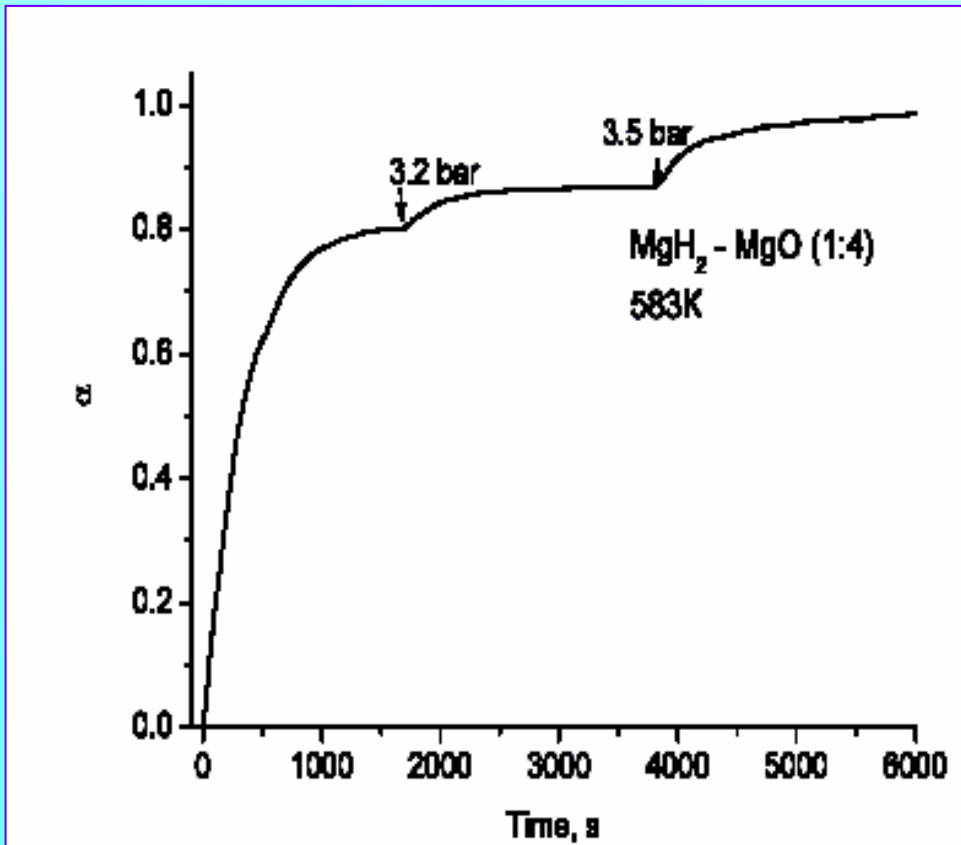
Peculiarities of hydrogen absorption by nanocrystalline Mg



Why reaction rate quickly decreases after achievement of the certain degree of transformation?

Why nanocrystalline magnesium is not completely transformed into magnesium hydride?

Dependence of reaction rate on hydrogen pressure at hydriding of nanocrystalline magnesium



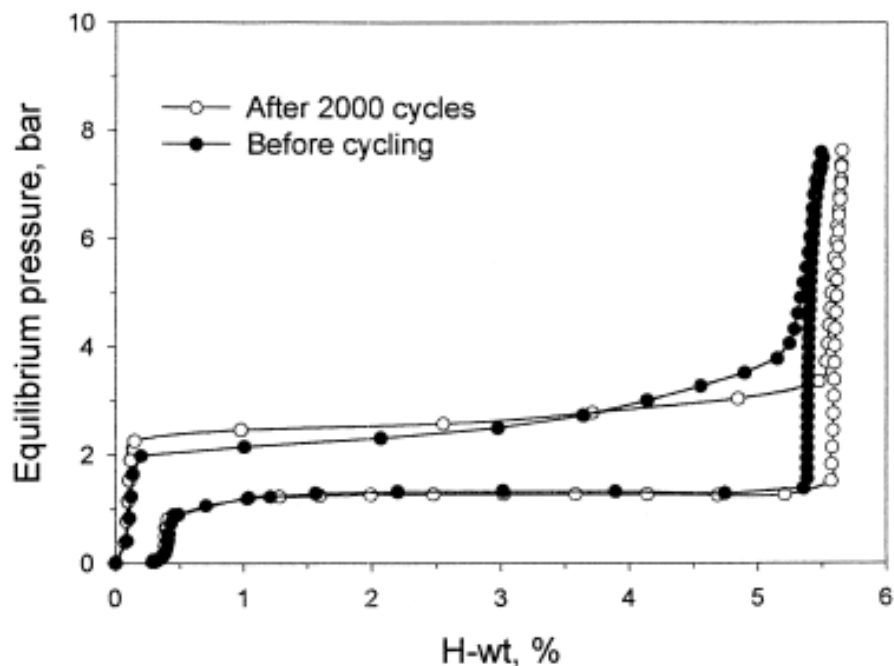
When reaction rate of hydriding becomes extremely low the dependence of reaction rate on pressure even is stronger ($V \sim \Delta P^n$) than linear ($V \sim \Delta P$)

How this phenomenon can be explained?

- $P_{eq} = 1.52 \text{ bar}$
- $\Delta P_1 = 1.48 - 1.28 \text{ bar}$
- $\Delta P_2 = 1.68 - 1.63 \text{ bar}$
- $\Delta P_3 = 1.98 \text{ bar}$

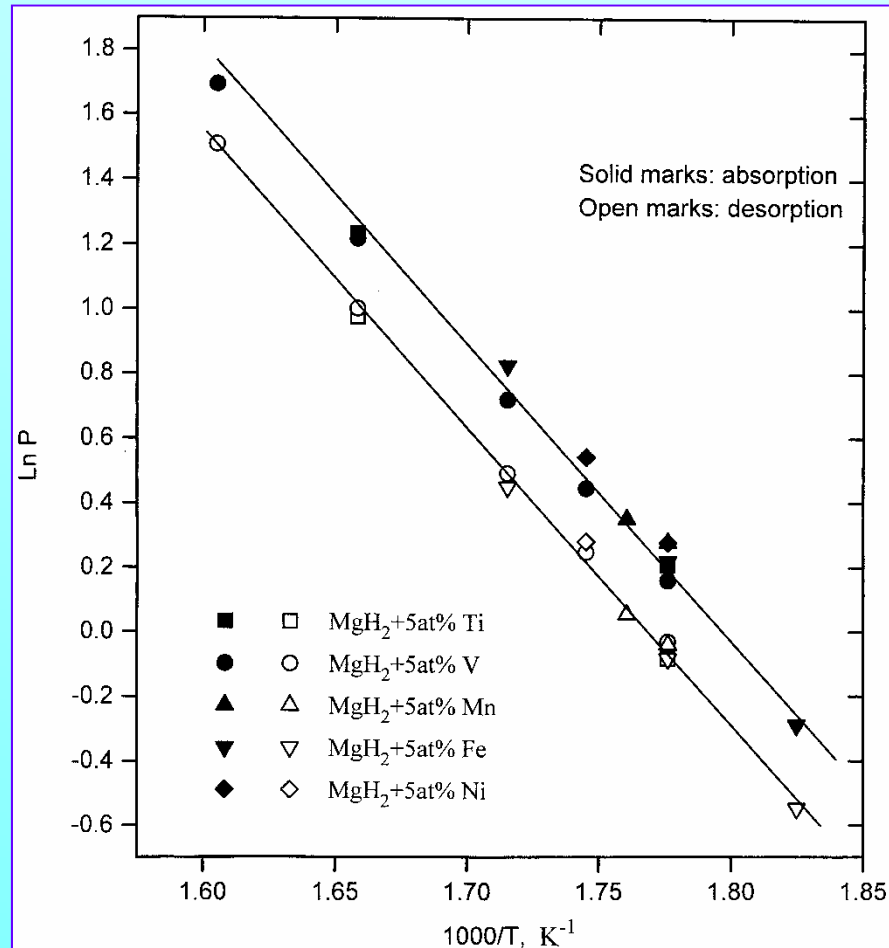
“Hysteresis”

Some authors reported about “hysteresis” phenomena observed at hydrogen interaction with nanocrystalline Mg-based systems



MgH₂ – 5at.% V, 300°C

Z. Dehouche, e.al., *J. Alloys & Comp.*, 305 (2000) 264



G. Liang et al, *J. Alloys Compd* 292 (1999) 247

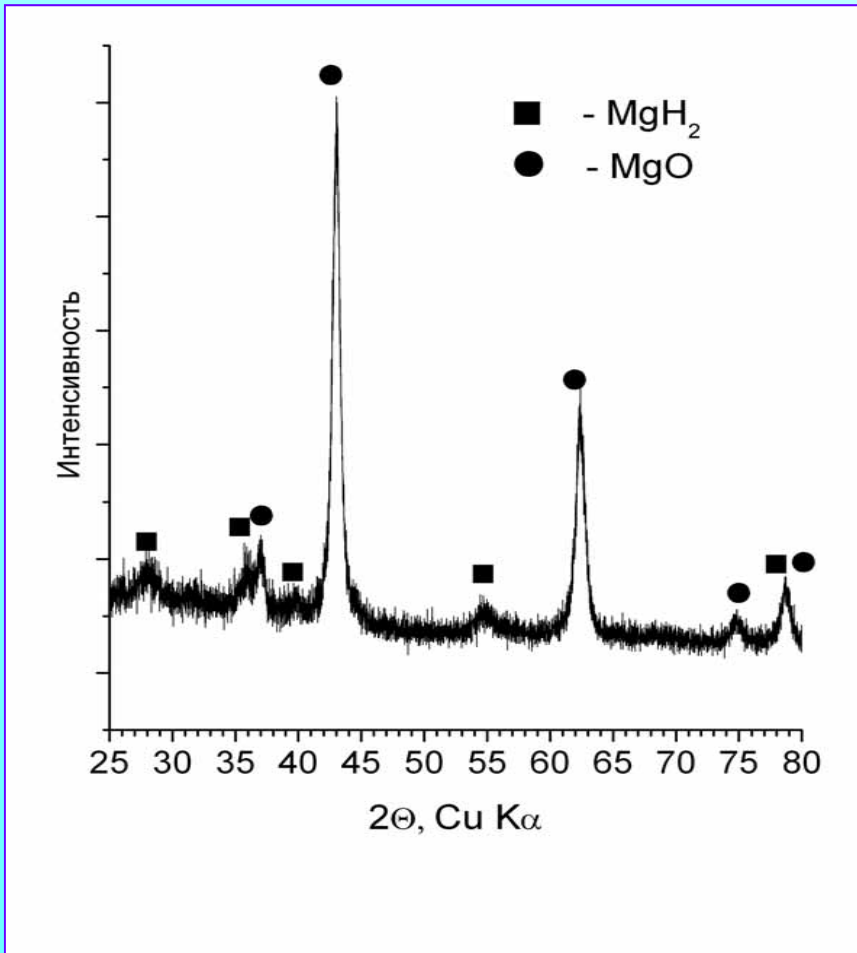
“Hysteresis”

Hysteresis is not observed for magnesium powders with an ordinary particles size (more than 1 μm) plateau slope $[\text{dlnP}/\text{d}(\text{H}/\text{M})]$ ($<1.5\%$).

Stampfer J.A. e.a., J.Am.Chem.Soc.,82 (1960) 3504-3508;
Vigeholm B. e.a., J.Less-Comm. Met., 89 (1983) 135-144;
Belkbir L., Int.J.Hydr.Energy, 6(1981) 285-294)

Is hysteresis a real phenomenon for nanocrystalline magnesium or not?

Preparation of nanocrystalline sample

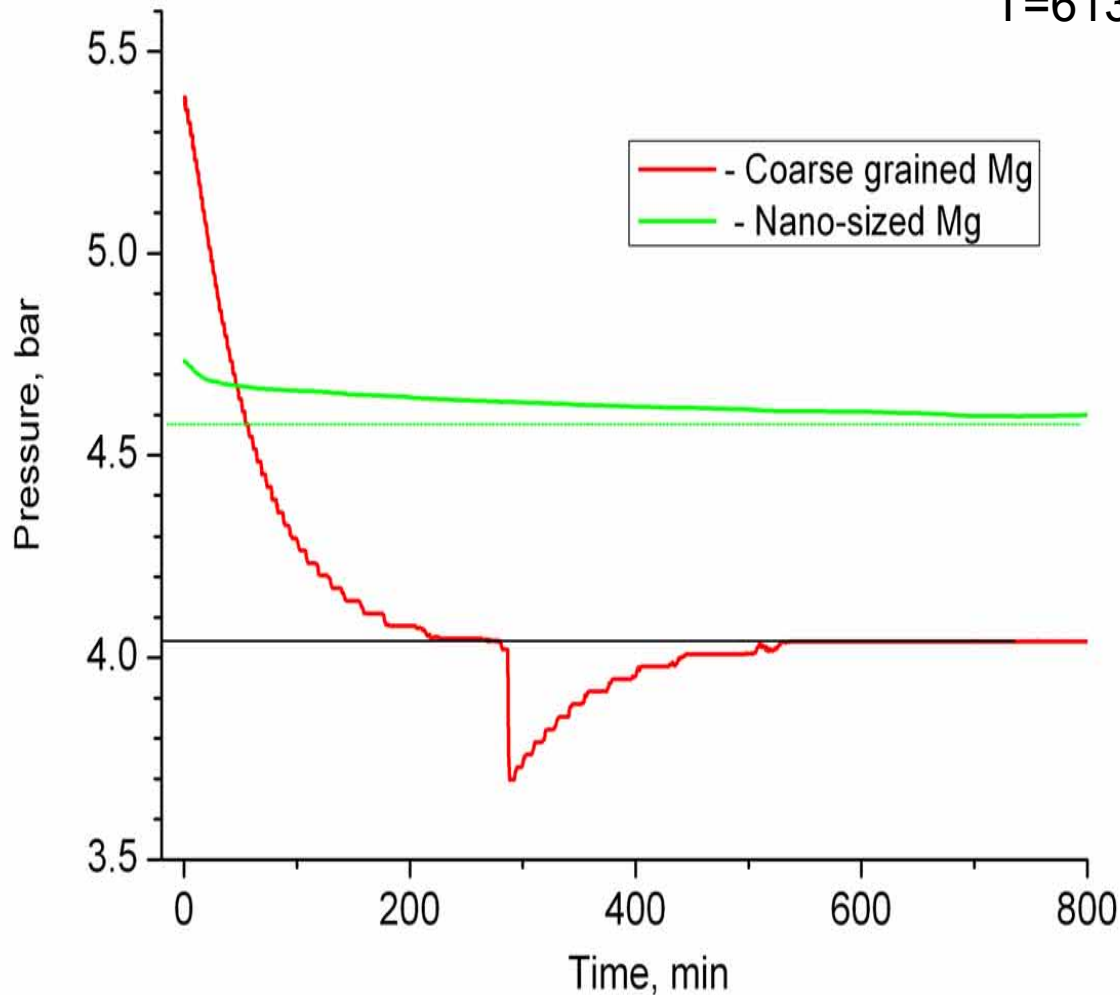


- Mixture MgH₂ + 80wt.%MgO was mechanically milled for 30 min
- MgO serves as a barrier preventing magnesium sintering
- coherent-scattering region for MgH₂ was 12 nm before hydriding experiment
- And 32 nm – after experiment

XRD pattern of the sample used in experiment

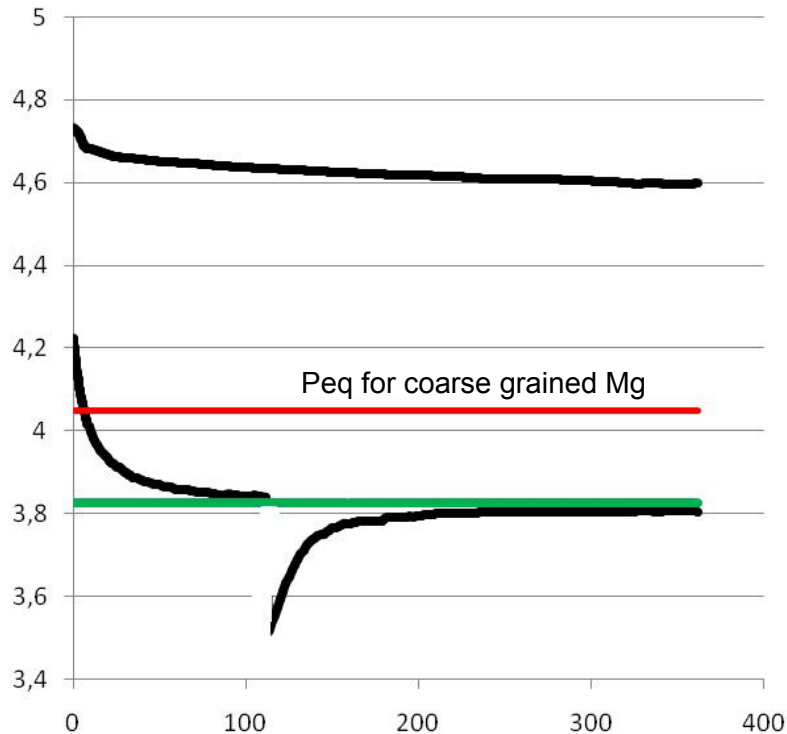
Approaching to equilibrium pressure by hydriding of coarse-grained and nanocrystalline magnesium

T=613 K



Coarse-grained magnesium reaches equilibrium hydrogen pressure (4.04 bar) for 5 h

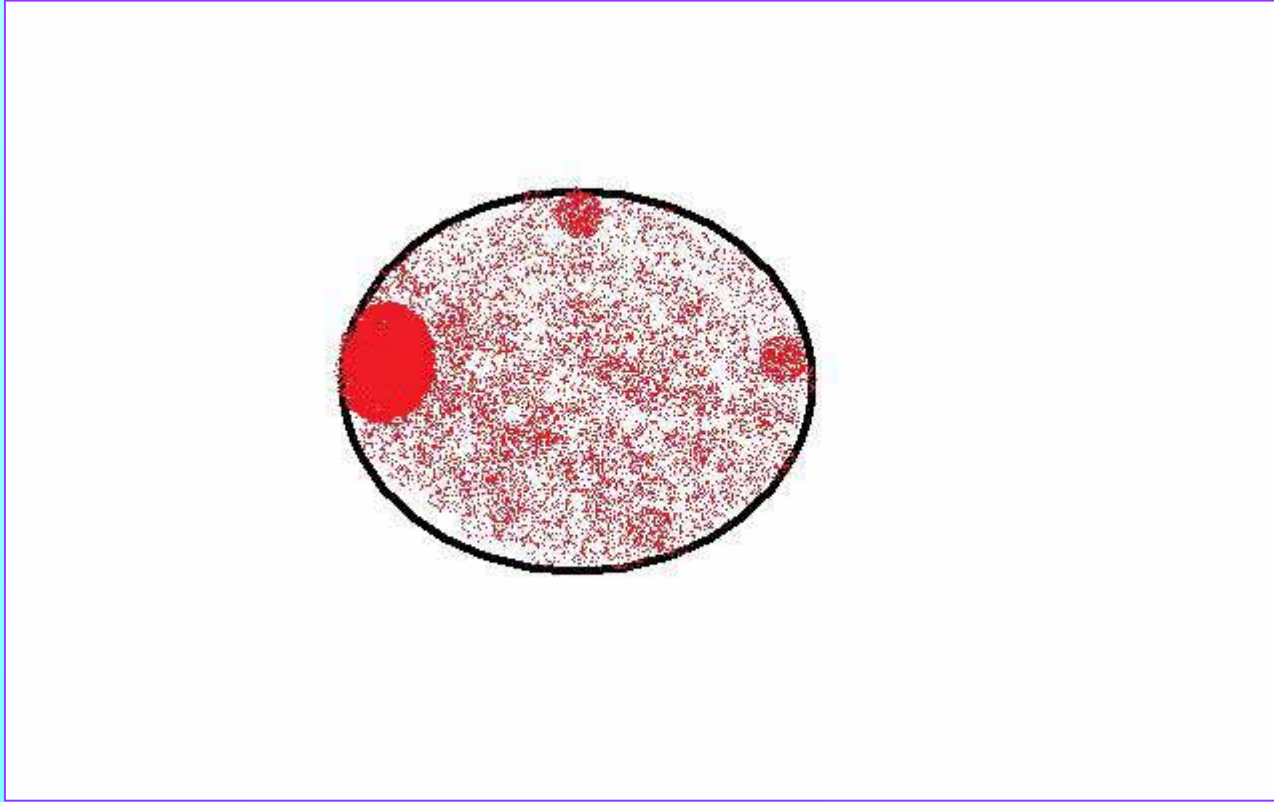
The zero-rate was not reached by nanocrystalline magnesium even for several days



It may be explained by very slow nucleation of magnesium hydride in nanocrystalline magnesium at hydrogen pressures close to equilibrium.

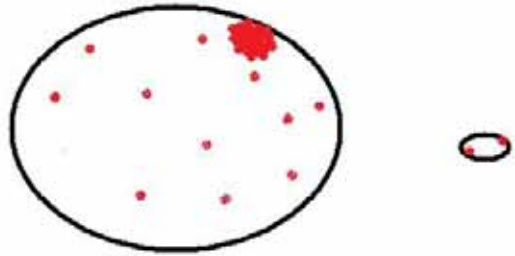
Initiation of nucleation by short increase of hydrogen pressure leads to approaching to equilibrium pressure for reasonable time.

How does hydrides nucleation proceed in metals?



1. Formation of a solid solution. Concentration of hydrogen solid solutions in metals $C_H \sim P^{1/2}$
2. Nuclei are formed as a result of decomposition of solid solution. A certain distribution of nuclei of different subcritical size which are in equilibrium with solid solution exists.
3. If addition of next atom (atoms) of H to nucleus does not disturb this quasi-equilibrium the nucleus becomes stable and freely growing. It means that certain supersaturation Δn is necessary for the formation of nucleus.

Why nucleation of MgH_2 is difficult in nano-sized particles?



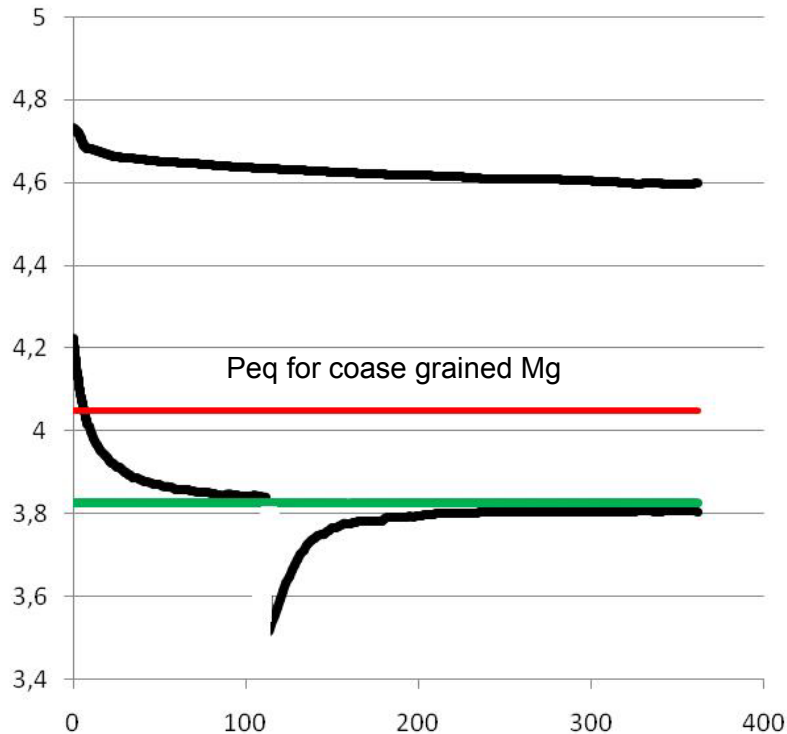
Solubility of hydrogen in magnesium is very low. Concentration H/M at 573 K and 1.47bar is estimated* to be $1.5 \cdot 10^{-4}$. It means that, for example, approximately 10-15 atoms of hydrogen are dissolved in particle with size of 15 nm ($\sim 70000 - 100\ 000$ Mg atoms).

**The estimation was done on the basis of data published in K.Zeng, e.a., "Critical assessment and thermodynamic modeling of the Mg-H system", Int. J. Hydr. Energy 24 (1999) 989-1004.*

It may be not enough for formation and growth of a critical nucleus in nano-sized particle.

If so, some part of nano-sized particles remains unreacted because a nucleus of magnesium hydride can not be formed.

Increase of solubility of hydrogen in magnesium (for example, by means of enhancement of hydrogen pressure) should increase the number of particles involved in reaction.

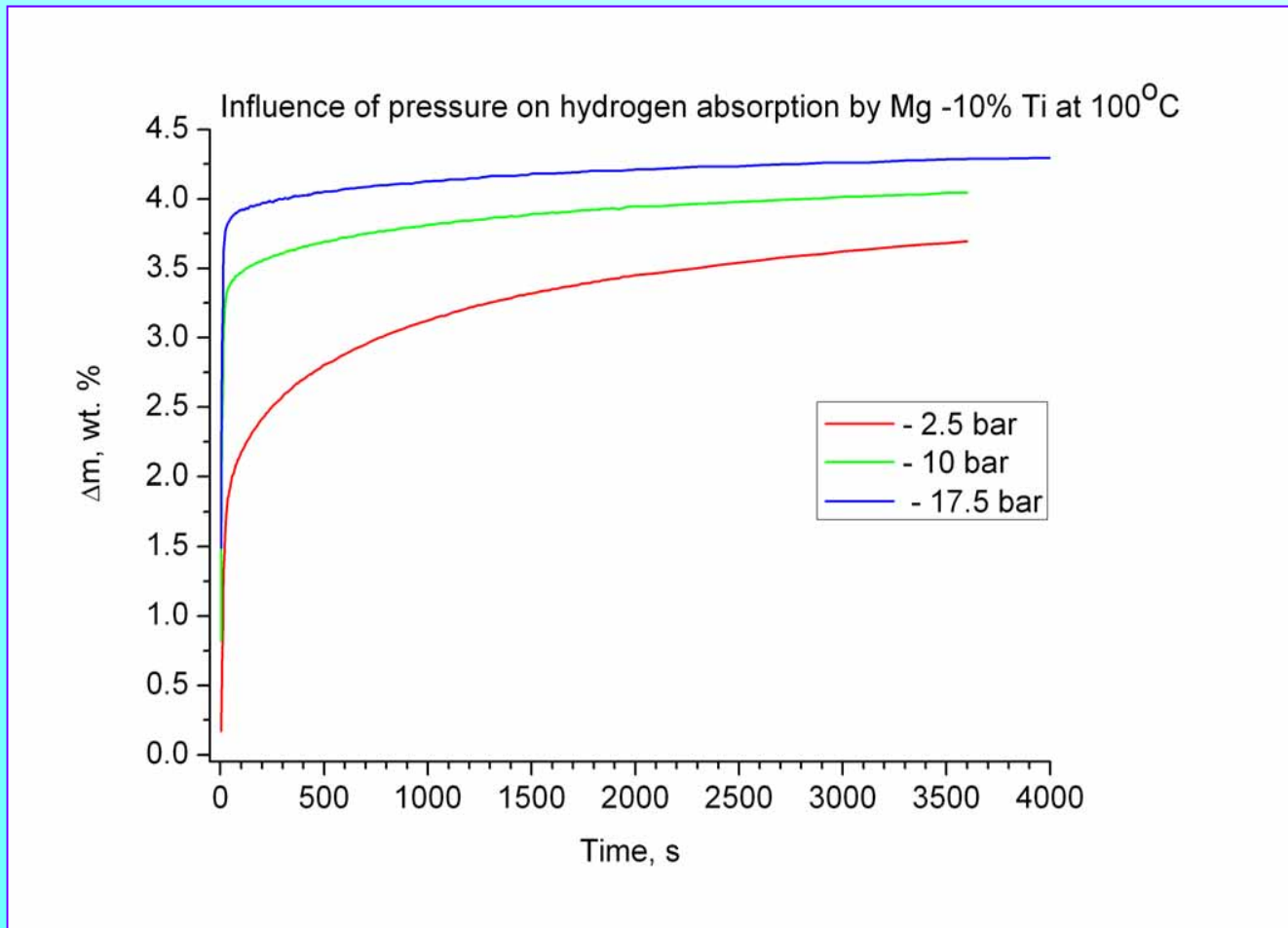


Short increase of hydrogen pressure leads to increase of concentration of hydrogen in nano-particles. Nuclei are formed, reaction proceeds at high rate and equilibrium is quickly reached.

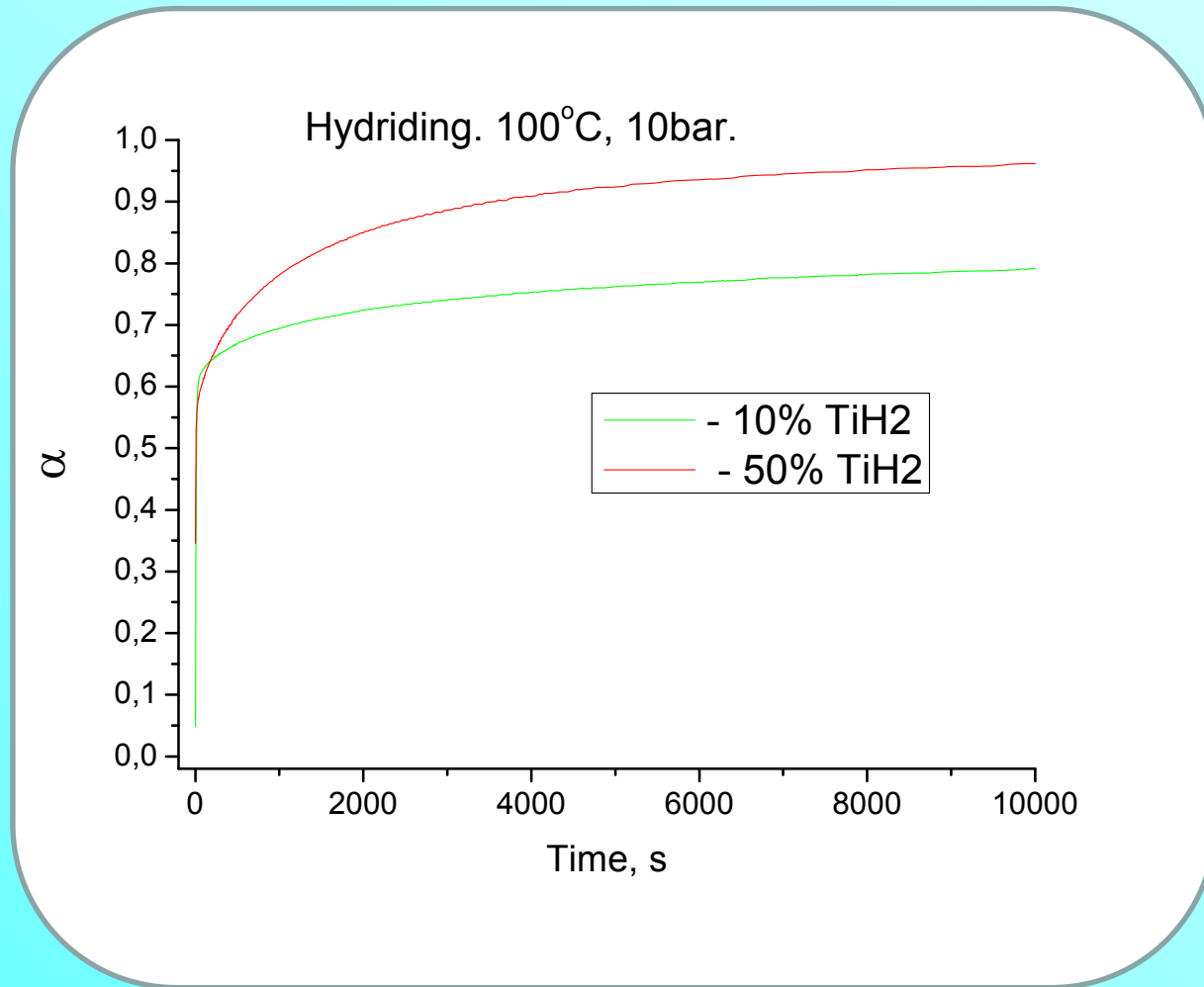
No difference between equilibrium hydrogen pressure obtained at hydrogen absorption and desorption is observed.

Equilibrium pressure for nano-sized Mg (15-50nm) is 5-25% lower, than that for common coarse-grained Mg. The most possible reason of it is the lesser surface energy of MgH_2 than Mg.

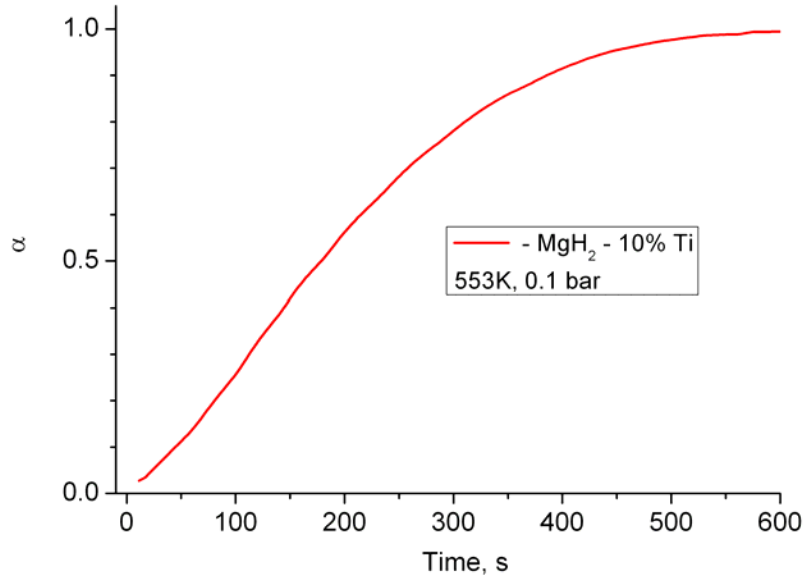
Increase of hydrogen pressure leads to higher hydrogen capacity



Facilitation of nucleation by increasing of catalyst's content leads to higher hydrogen capacity

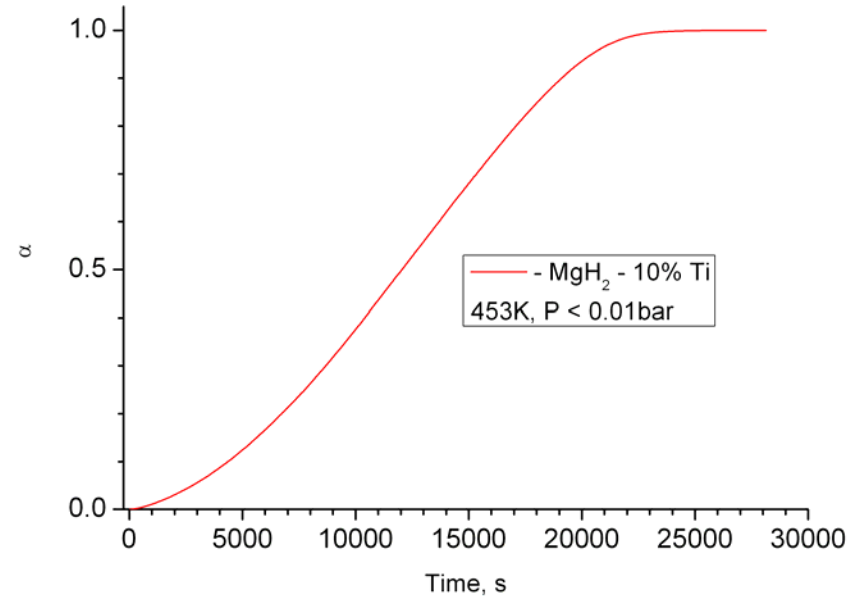


Dehydrating



Nanocrystalline MgH_2 remain too stable.

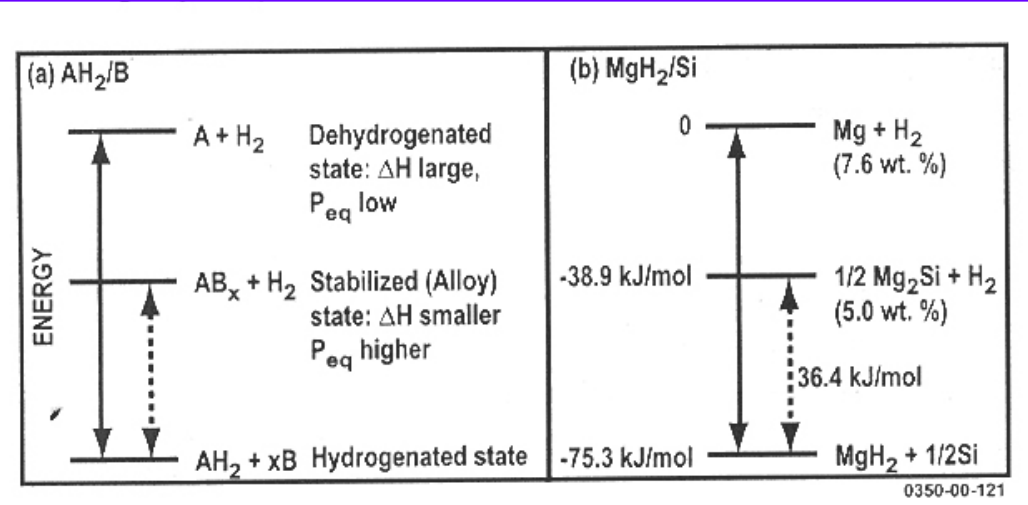
A reasonable rate of dehydrating at pressures higher than 1 bar can be achieved **only at elevated temperatures** ($>300^\circ\text{C}$)



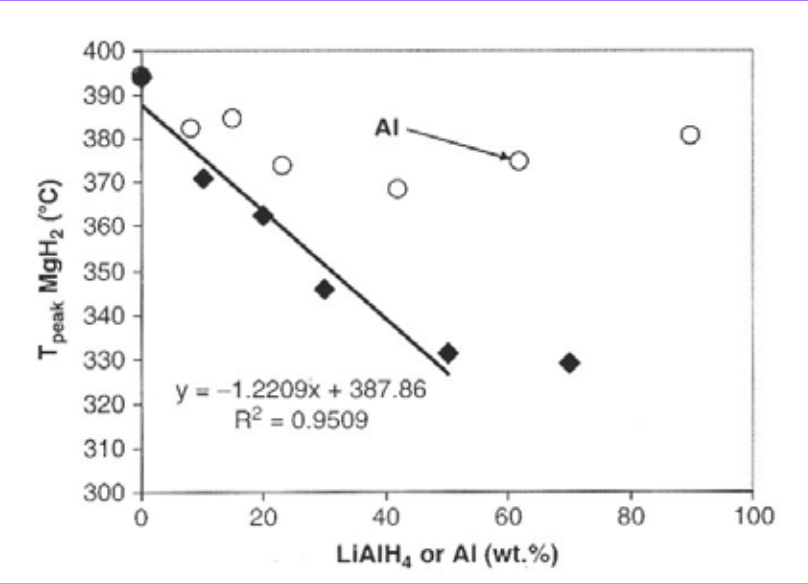
Destabilization of magnesium-based hydrides

- ◆ **Reactive mechanical milling (activation) of MgH₂**
- ◆ **Decrease of enthalpy of dehydriding by means of compositing with additives changing the reaction products**
- ◆ **Substitution of elements in intermetallic compounds**
- ◆ **Search for new hydrides**

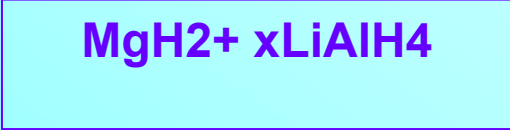
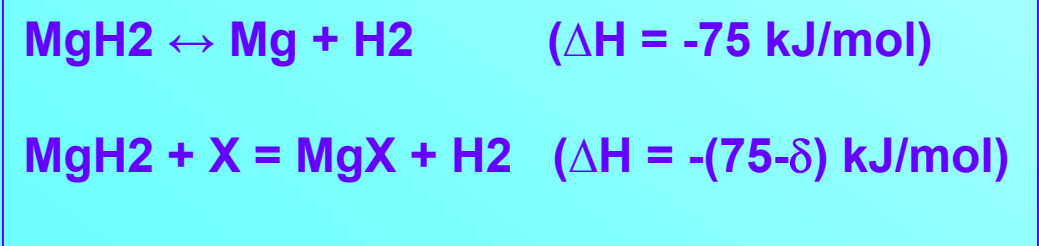
Decrease of enthalpy of dehydrating by means of compositing



J.J.Vajo et al, J. Alloys Compd, 446-447 (2007) 409

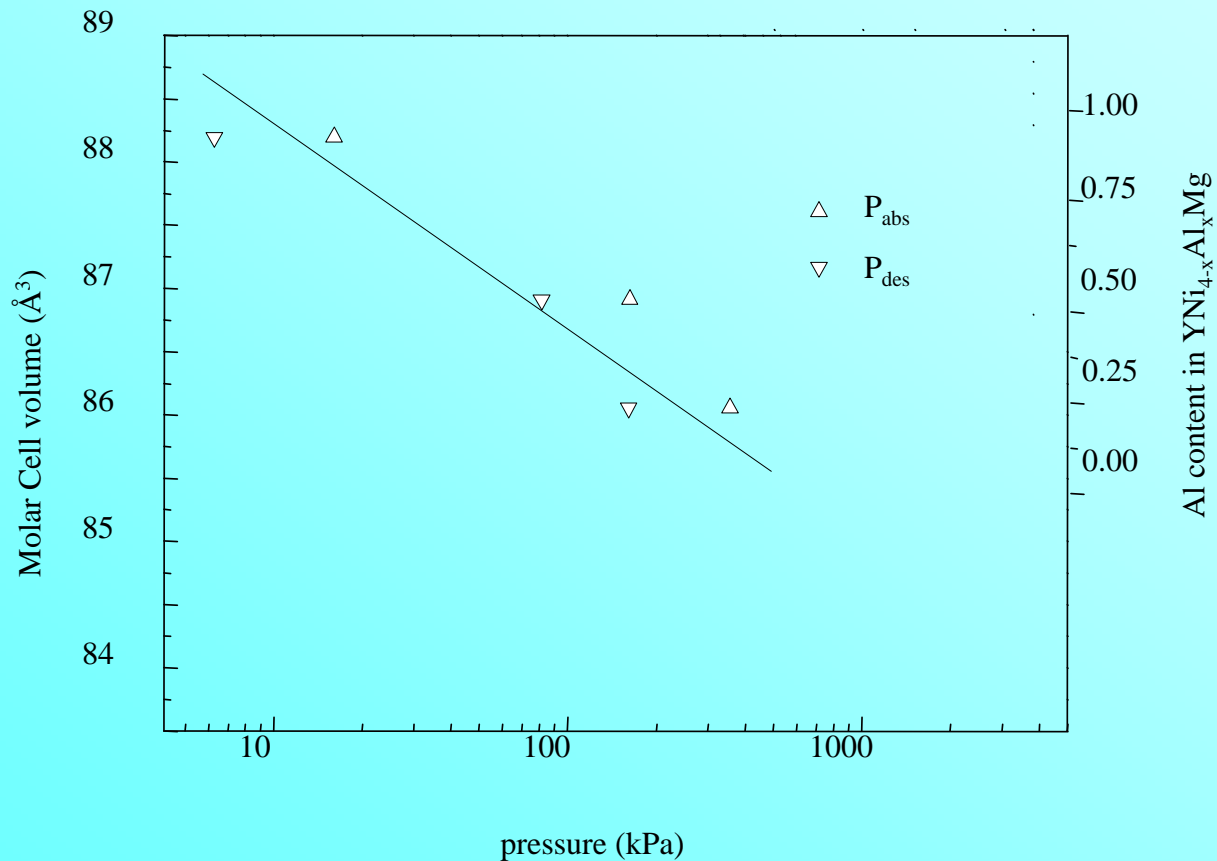


R.F.Varin "Nanomaterials for Solid state Hydrogen Storage"



According to DSC study the temperature of decomposition of MgH_2 decreases with increase of $LiAlH_4$ content, but hydrogen capacity of the mixture does not exceed pure $LiAlH_4$

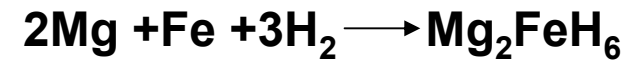
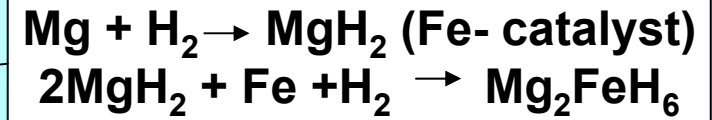
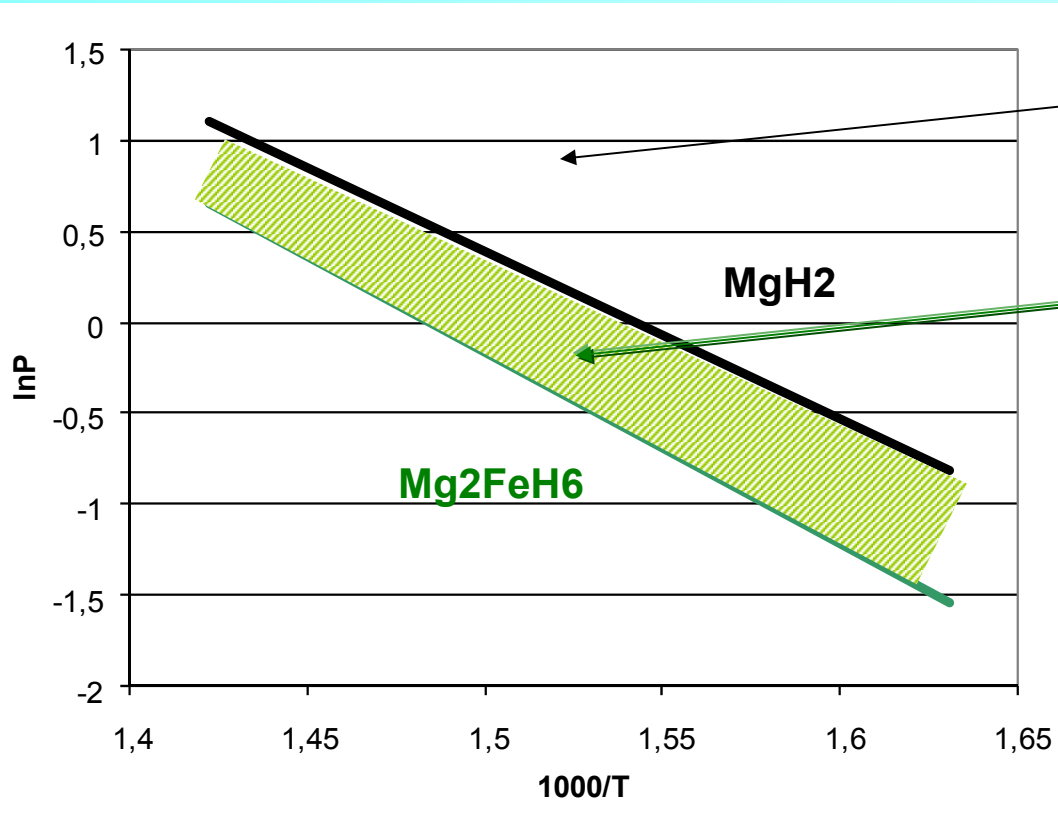
The alteration of the equilibrium plateau pressure by partial substitution of elements in intermetallic compounds



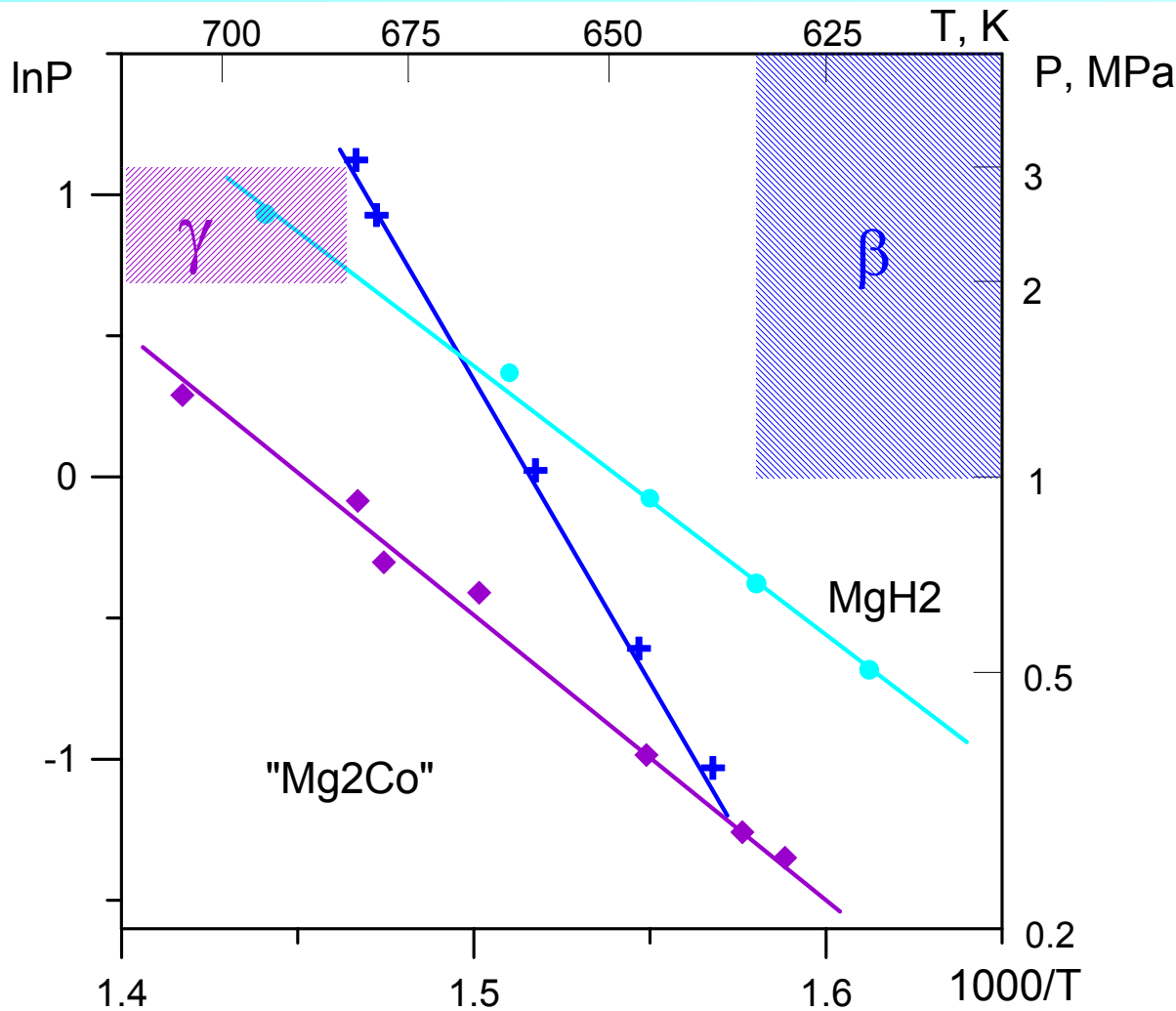
Dependence of the equilibrium plateau pressure as a function of the lattice parameters in $\text{YNi}_{4-x}\text{Al}_x\text{Mg}$

Mechanical alloys as precursors in synthesis of new hydrides

Mg and Fe are immiscible metals



Mechanical alloys as precursors in synthesis of new hydrides

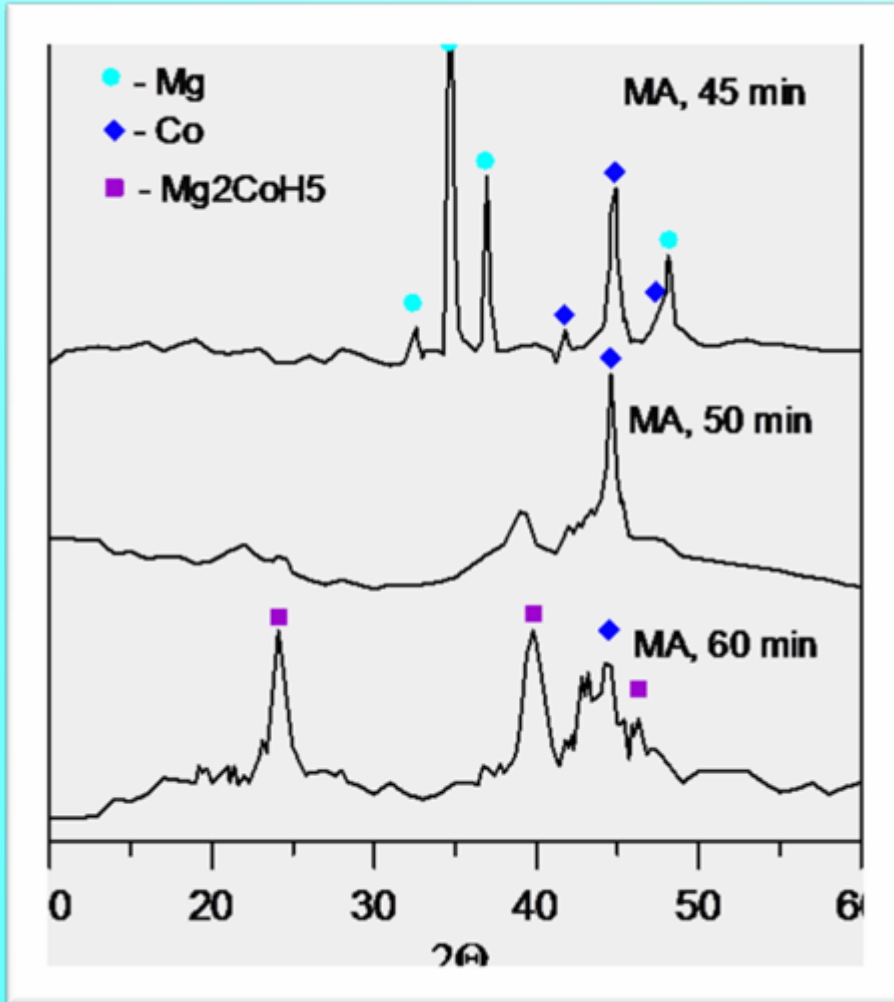


Two ternary hydrides (Mg_2CoH_5 and Mg_3CoH_5) and one intermetallic compound (Mg_2Co) have been obtained by means of hydriding of Mg-Co mechanical alloys.

β - tetragonal Mg_2CoH_5

γ - orthorhombic Mg_3CoH_5 ($Mg_6Co_2H_{11}$)

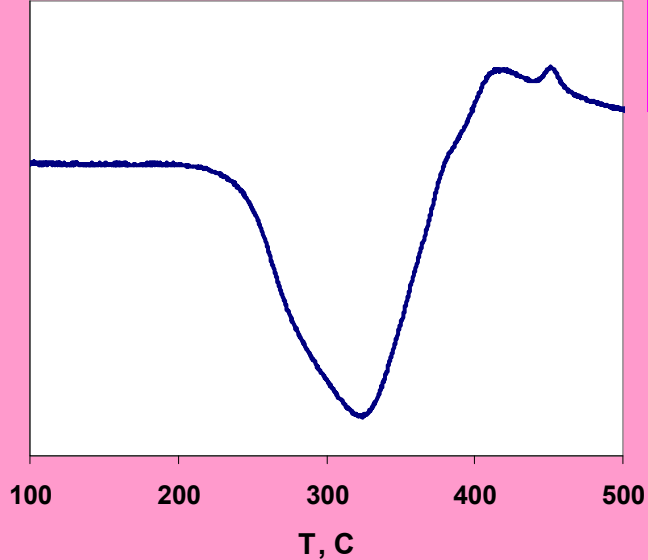
Reactive mechanical alloying



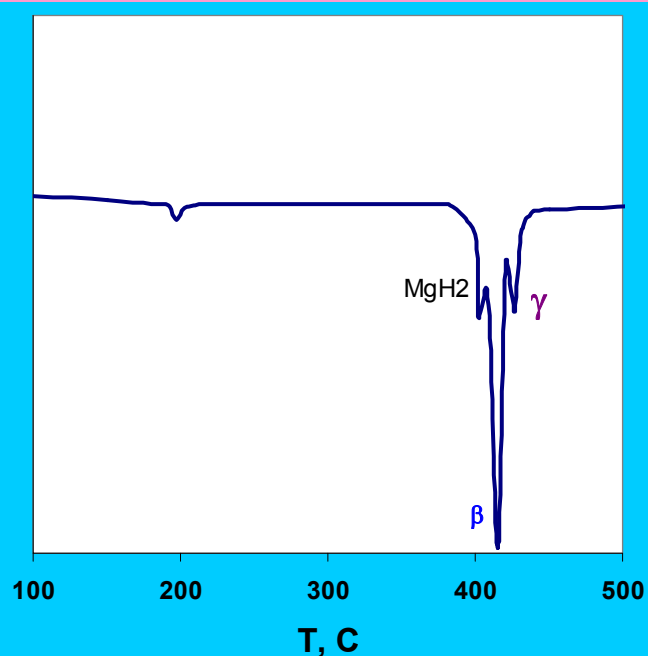
The process similar to self-propagating high-temperature synthesis (SHS) had been observed during mechanical alloying of magnesium and Co under hydrogen atmosphere

Reactive mechanical alloying

DTA curve of 2Mg+Co sample mechanically alloyed in hydrogen atmosphere at acceleration 40g for 50 min.



The product formed as a result of SHS-like process contains hydrogen and seems not to be a mixture of phases. Only one rather broad peak can be observed on DTA curve at its decomposition. More probably this product is an amorphous phase containing hydrogen in various positions with different bonding energy.



β - tetragonal Mg_2CoH_5

γ - orthorhombic Mg_3CoH_5 ($Mg_6Co_2H_{11}$)

DTA curve of separately hydrided 2Mg+Co mechanical alloy

CONCLUSIONS

- ◆ The composites with homogeneous phases distribution and large interface area (so called “mechanical alloys”) formed at the mechanical alloying of metal powder mixture or mixture of metal with other additives possess improved reactivity towards hydrogen.
- ◆ Mechanical alloying is almost unique method of fabrication of composites from immiscible components. This opens the possibility for synthesis new hydrides phases.
- ◆ Surface-active additives to magnesium can promote pulverization of metal and modify its surface. This leads to increase of hydrogen capacity.
- ◆ Nanostructural composites can be obtained at mechanical alloying of MgH_2 with additives. These composites after preliminary dehydriding very easily react with hydrogen even at temperature as low as 373-473 K and reach hydrogen capacity higher than 4 wt.%. The hydrogen capacity close to 7 wt/% can be achieved at 623 K

CONCLUSIONS

- ◆ Hydriding properties of nanocrystalline magnesium possess some peculiarities which should be taken into consideration at investigation and development of nanostructural hydrogen storage materials.
- ◆ Due to very low solubility of hydrogen in magnesium the nucleation processes play even more important role in hydriding of nanocrystalline Mg than of coarse-grained Mg.
- ◆ It may explain the «hysteresis» phenomenon reported by some authors for nanocrystalline magnesium-based systems. Actually, there is no hysteresis in the interaction of Mg with hydrogen. The apparent «hysteresis» is caused by a hampered nucleation of MgH₂ in nano-sized particles at a hydrogen pressure near equilibrium pressure.
- ◆ Equilibrium pressure for nanocrystalline Mg is lower, than for coarse-grained Mg. The most possible reason of it is the lesser surface energy of MgH₂ than Mg.

CONCLUSIONS

- ◆ The hampered hydride nucleation in nanocrystalline particles may lead to a decrease of total hydrogen capacity because some particles remain unreacted.
- ◆ Facilitation of hydride nucleation leads to an increase in the number of particles involved in the reaction and consequently an increase in total hydrogen capacity.
- ◆ The carrying out of mechanochemical processes under a hydrogen atmosphere can lead to the formation of hydrides directly in the course of mechanical alloying (the so-called “reactive mechanical alloying”). As a rule, the phases formed in such a way are metastable in their nature and possess properties that are interesting and different from conventional phases.
- ◆ Metallic contaminations that arise as a result of mechanical treatment do not negatively affect hydriding and dehydriding and even can accelerate these processes. It makes mechanical alloying very convenient for the fabrication of hydrogen storage materials in contrast to many other technologies where contaminations by materials of balls and vials is a serious problem.

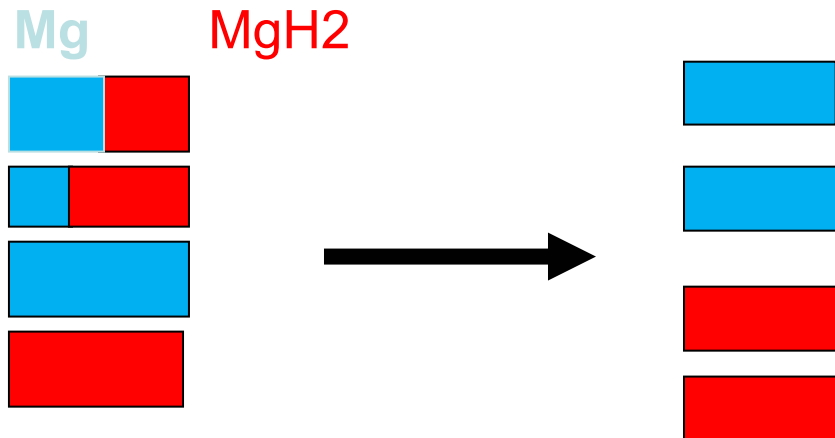
Thank you for attention

What may be the cause of decreasing of equilibrium hydrogen pressure for nanocrystalline Mg ?

- $RT \ln P_{eq} = \Delta H - T \Delta S$
- $\Delta H = \Delta H_{bulk} + S_{Mg} \sigma_{Mg} - S_{MgH_2} \sigma_{MgH_2}$
- Equilibrium pressure for nano-sized Mg (15-50nm) is 5-25% lower, than that for common coarse-grained Mg.
- This decrease corresponds to increase in ΔH by $\sim 0.4 - 1.2$ kJ/mole.
- $\sigma_{Mg} = 600$ mJ/m². σ_{MgH_2} is unknown. Surface energy of magnesium particle with diameter of 15nm is equal 3.4kJ/mole. σ_{MgH_2} should be less than σ_{Mg} by ~ 200 mJ/m².
- Is such relation between surface energy of Mg and MgH₂ reasonable? As a rule a surface energy of a metal is sufficiently larger than that of it's binary compound. Data for Zr illustrate this regularity.
- | | Zr | ZrO ₂ | ZrC |
|-------------------------------|------|------------------|-----|
| σ (mJ/m ²) | 1400 | 600 | 800 |

Explanation:

1. Near equilibrium the kinetics of magnesium hydriding is being determined by the nucleation of MgH_2
2. Particles in which the nucleus of MgH_2 is formed are quickly transformed into hydride whereas the others are still unreacted towards hydrogen

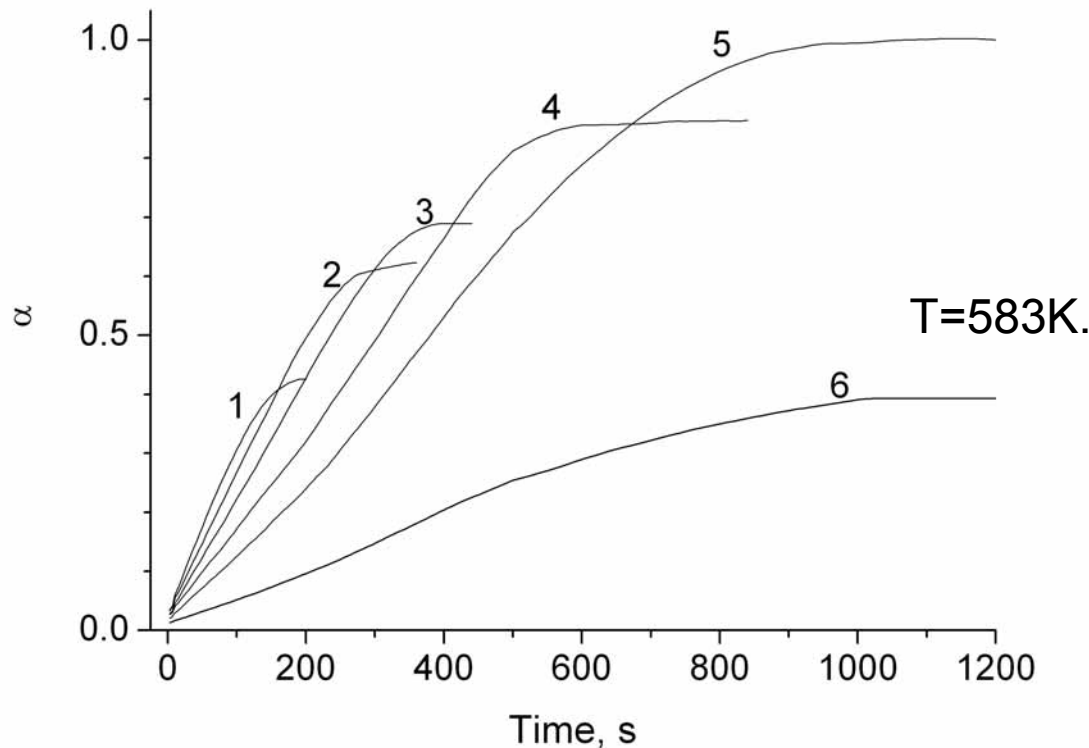


Far from equilibrium –
the reaction proceeds
with appreciable rate

Near equilibrium –
the reaction rate is
very slow

3. Because of hampered nucleation nanocrystalline magnesium sample mainly consists of two types of particles: Mg and MgH_2 . There are almost not particles with Mg/ MgH_2 interface near equilibrium

Experimental evidence of explanation



α - relation of quantity of the hydrogen evolved at dehydriding to quantity of hydrogen absorbed at full hydriding .

Dehydriding rates of MgH_2 - 80% MgO milled blend hydrided up to different reaction fraction.

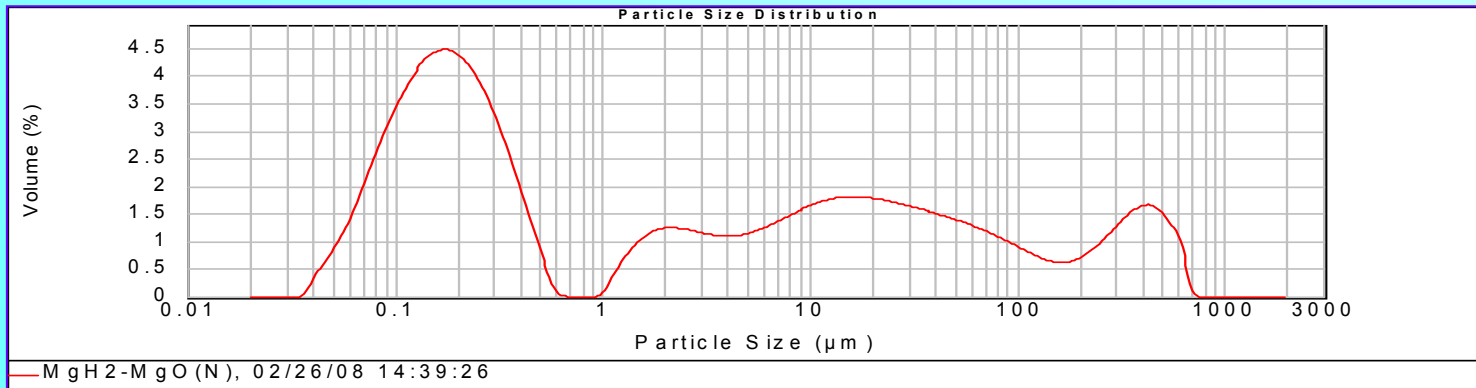
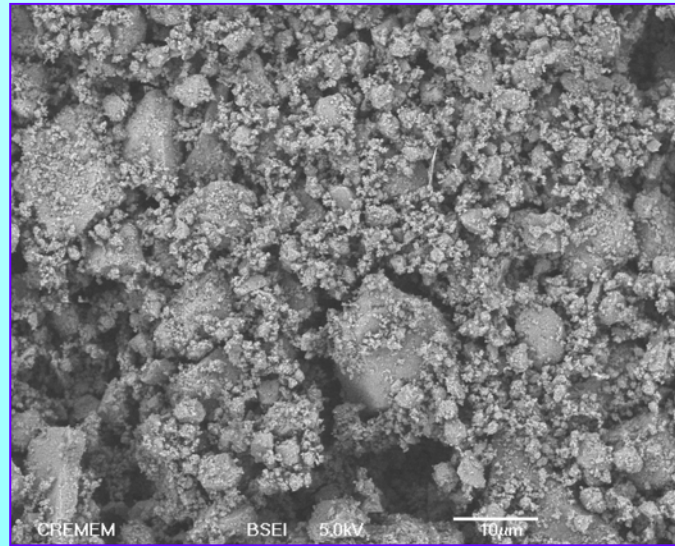
In the case of curve 6 hydriding was near the equilibrium.

The maximum rate of decomposition are noticeably lower for curve 6 than this for curve 1, while the amount of Mg transformed into MgH_2 for these curves is almost the same.

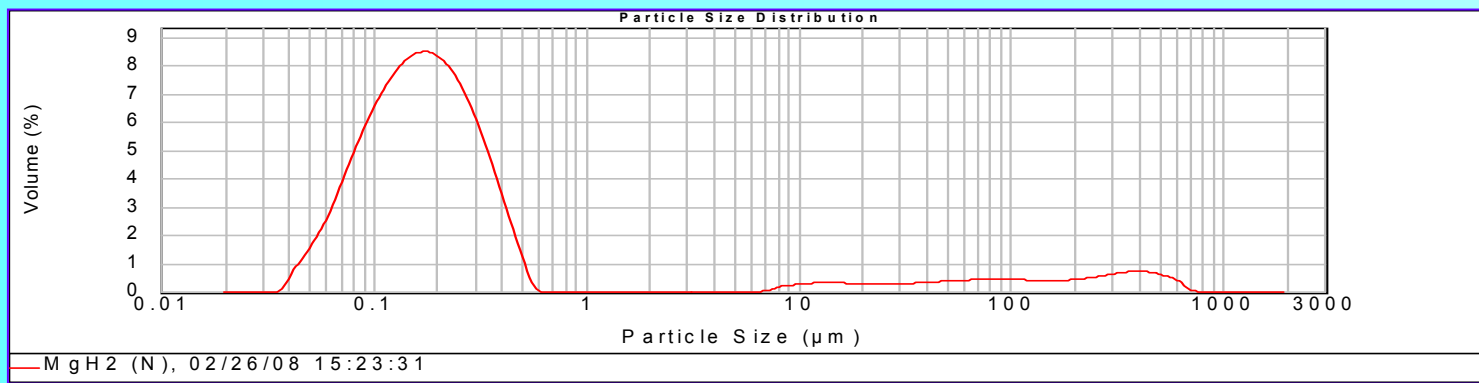
Curve 6 can be affinely transformed into curve 5 for completely hydrided powder

This means that particles partially converted into hydride are absent in the sample hydrided near equilibrium like in the case of completely hydrided powder.

Characterization of BM sample MgH₂+MgO



MgH₂+MgO



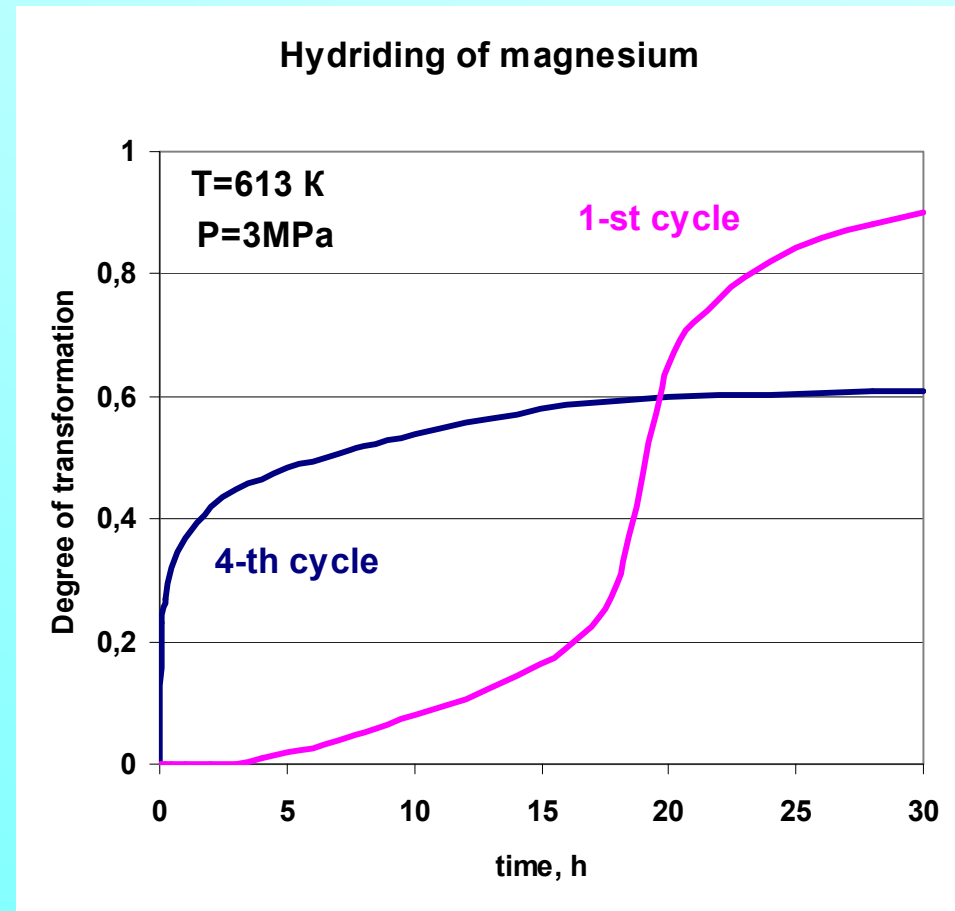
MgH₂

Peculiarities of magnesium hydriding

Kinetics of magnesium hydriding in the first and the subsequent cycles essentially differs.

The overall kinetics of first hydriding of magnesium is determined by the statistical cracking of an oxide layer (owing to different coefficients of thermal expansion of Mg and MgO) and hydride nucleation on the metal sites formed. This leads to a long induction period and sigmoid shape of the kinetic curve.

The rate of magnesium hydriding at the initial stages of second and subsequent cycles is limited by the dissociative adsorption of hydrogen on the metal surface. The nuclei of magnesium hydride are formed on the metal surface, with an interface propagating along the metal surface. The overlap of nuclei leads to formation of a “surface shell” of magnesium hydride which blocks further hydrogen uptake.



Requirements

