

# PECULIARITIES OF HYDROGEN INTERACTION WITH NANOCRYSTALLINE MAGNESIUM

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## Introduction

In recent years the main tendency in improving hydriding properties of magnesium consists in fabrication of nanocrystalline magnesium-catalyst composites. As a rule, it significantly accelerates hydriding and dehydriding rates. But some peculiarities in hydriding properties of nanocrystalline magnesium have been revealed and they should be taken into consideration at investigation and development of nanocrystalline hydrogen storage materials.

For example, some authors reported about "hysteresis" phenomenon observed in nanocrystalline Mg-based system [1-4], which is not observed for magnesium powders with an ordinary particle size (more than 1  $\mu\text{m}$ ). A stronger dependence of reaction rate on hydrogen pressure was observed for hydriding of nanocrystalline magnesium in comparison with coarse-grained magnesium. The question remains why nanocrystalline magnesium is not completely transformed into magnesium hydride.

In this work some explanations of observed phenomena are proposed on the basis of role of nucleation processes in hydriding of nanocrystalline magnesium.

## Results and discussion

It has been revealed that the nucleation processes play even a more important role in hydriding of nanocrystalline Mg than in hydriding of coarse-grained Mg. Due to very low solubility of hydrogen in magnesium, the number of hydrogen atoms dissolved in nano-sized particle of magnesium may be not enough for formation and growth of a critical hydride's nucleus.

It may explain the «hysteresis» phenomenon. We have shown that there is no hysteresis in the interaction of nanocrystalline Mg with hydrogen. The apparent «hysteresis» is caused by a hampered nucleation of  $\text{MgH}_2$  at a hydrogen pressure close to equilibrium pressure. Initiation of nucleation by short increase of hydrogen pressure leads to approaching the equilibrium pressure which is the same as obtained in dehydriding process.

Equilibrium pressure for nano-sized Mg turns

out to be lower, than for coarse-grained Mg. The most possible reason of this is the lesser surface energy of  $\text{MgH}_2$  than Mg.

The kinetic curves of hydriding of nanocrystalline magnesium are not fitted by any formal reaction rate expression usually used for the analysis of heterogeneous reactions. The shape of the curves also differs from the shape of hydriding curves of ordinary magnesium. The reaction rate quickly decreases after achievement of the certain degree of transformation. This leads to incomplete transformation of magnesium into hydride (Fig. 1).

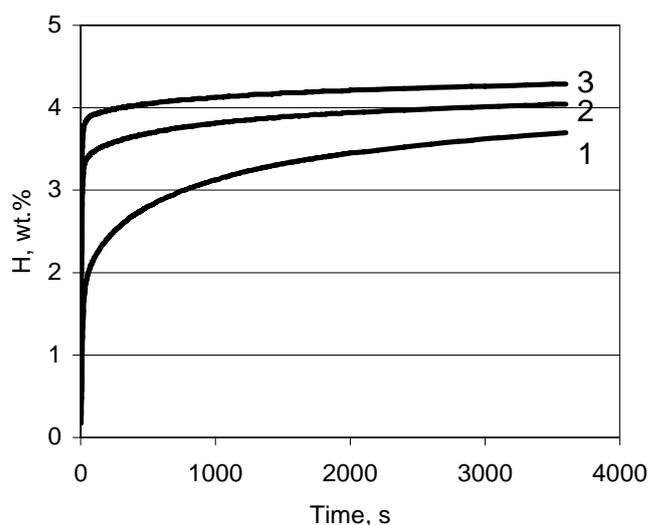


Fig.1. Influence of pressure on hydrogen absorption by Mg-10%TiH<sub>2</sub> nanocrystalline composite at 100°C.

1 – P=2 bar, 2 – P=10 bar, 3- P=17.5 bar.

This phenomenon also can be explained by hampered hydride nucleation in nano-sized particles because some particles remain unreacted.

A possible way to increase hydrogen capacity of nanocrystalline magnesium can be found in facilitation of nucleation processes. It can be achieved by increase of solubility of hydrogen in magnesium (for example, by means of enhancement of hydrogen pressure), by the artificial nucleation with the help of "hydrogen sources" (such as other hydrides, for example) or by creation of conditions for cooperative action of

nano-sized particles when dissolved hydrogen can readily diffuse from one particle to another to form hydride nucleus. Figures 1 and 2 can serve as illustrations of this statement.

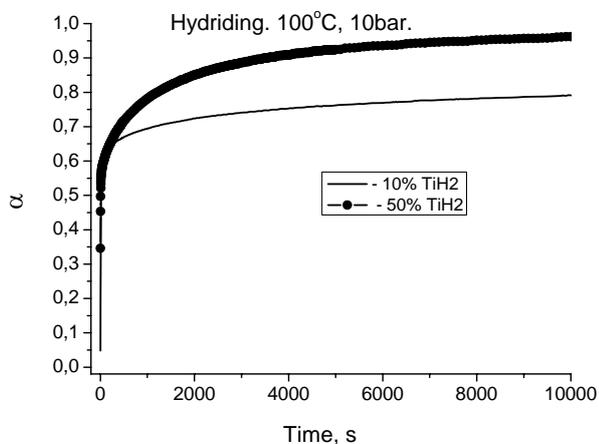


Fig. 2. Increase of degree of transformation of Mg into hydride with the increasing of content of TiH<sub>2</sub> in Mg-TiH<sub>2</sub> nanostructural composite.

### 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 MgH<sub>2</sub> in nano-sized particles at a hydrogen pressure near equilibrium pressure.

Equilibrium pressure for nanocrystalline Mg is somewhat lower, than for coarse-grained Mg. The most possible reason of it is the lesser surface energy of MgH<sub>2</sub> than Mg.

The hampered hydride nucleation in nano-sized particles may leads to decrease of total hydrogen capacity because some particles remain unreacted.

A possible way to increase hydrogen capacity of nanocrystalline magnesium can be found in facilitation of nucleation processes. It should increase the number of particles involved in reaction and consequently increase total hydrogen capacity.

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