

PROBLEMS OF FAST ABSORPTION AND DESORPTION OF HYDROGEN BY METAL HYDRIDES

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Introduction

A purposeful optimization of hydride forming metals and alloys is of great technological importance in order to obtain fast absorption and desorption of hydrogen in metal-hydrides storage devices, to extend its resource. This hardly can be done without detailed understanding of mechanisms of hydrogen uptake and release from metal hydrides. In our report we present the results of experimental and theoretical study of the kinetics of hydrogen sorption and desorption by metal hydrides. Also some possibilities of their optimization are discussed.

Numerous attempts to improve kinetic parameters of metal-hydride materials were made during a long time by several ways: covering by surface catalysts including oxides and graphite, forming composites, chemical modification using organic materials, ball-milling and so on (see, for example [1-4]). However it is too soon to consider these efforts as systematic.

This work presents the results of experimental and theoretical study of the kinetics of absorption and desorption of hydrogen by metal hydrides and considers some possibilities of their optimization taking into account effects of rates of the transport of hydrogen through a surface and in a bulk of a material. Modification of chemical and structure properties due to a composite formation is not considered.

Details of the method

Studies have been carried out by means of comparison of experimental results to mathematical models.

Mathematical modeling was developed not by means of searching limiting stages but taking concurrently into account all elementary processes of hydrogen transport in metal and hydride phases. We analyzed the following reactions, which influence hydrogen uptake and release:

- nucleation of a new phase (separately of growth),
- growth of nuclei,

- absorption and desorption by surfaces of metal and hydride phase,
- diffusion of hydrogen in metal bulk and in hydride phase,
- formation/ decomposition of hydride phase.

Adequacy of the presented models was tested by their ability to fit experimental data. Using mathematical modeling and fitting allow obtaining evaluations of the rate constants, suitable for engineering calculations.

The experimental results have been obtained using TDS, barometric method, and thermocycling method. We studied powders, obtained as a result of numerous cycles of hydrogenation/ dehydrogenation. Special attention was paid to the temperature control of the samples.

Results and discussion

Two types of metal hydrides (with metallic and ion-covalent bonding) have different peculiar properties of hydrogen transport. Therefore, the mathematical models for them are different. These peculiarities result from the differences in the electronic structure of the materials. In particular, non-metal materials have significantly lower diffusivity of hydrogen and adsorption/desorption rates compared to metals. The problem is that the limit hydrides of metals (presenting the largest practical interest) are generally non-metals that adversely affects on the kinetics of hydrogen uptake and release.

Many factors influence the rates of hydrogen uptake and release by hydrides of metals. We have analyzed the following factors and ways of their optimization.

Uptake of hydrogen

- The cleanness of a surface of powder samples is of great importance for the absorption rate for hydrides with metallic type of bounding. Diffusivity is high enough even at moderate temperatures and do not influence on uptake of hydrogen in small-size particles of a powder.
- While hydrogen is adsorbed the intensive formation of a hydride phase starts after the nuclei have appeared. In some cases the probabili-

ty of appearance of nuclei may be increased using catalytically active coverings.

- The nuclei growth stage doesn't slow down hydrogen uptake almost up to formation of the skin of the new phase.
- Low diffusivity of hydrogen in the hydride phase with ion-covalent bonding significantly decreases the rate of uptake after the hydride skin has been formed. This may give explanation to the very slow rates of hydrogenation of, say, magnesium on final stages of the hydride forming. It is possible to make hydrogenation faster by reducing the diffusion paths, i.e. by pounding the hydride powder.
- *Release of hydrogen*
- Even at moderate temperatures the rate of hydrogen release from metal hydrides with metallic bounding is generally determined by the desorption rate, which depends on how clean the surface is. On final stages a rate of hydrogen release from such objects may be limited by a rate of decomposition of hydride phase.
- Since a rate of desorption of hydrogen from hydride with ion-covalent bounding is usually very low, a heating to considerable temperatures is needed for producing release of first portions of hydrogen. After the nuclei of metal phase are formed they open a way to the "fast" desorption. Through these channels that become more and more large the intensive release of a rest of hydrogen from metal hydride occurs. The covering of a surface of such metal hydrides by catalytically active layers may lower activation barriers for desorption of first portions of hydrogen. In that way the initial temperature of desorption may be brought down.

- The size distribution of the particles of the hydride powder influences the rate of hydrogen desorption. Narrow size distribution (which can be obtained by, e.g., sifting) notably increases the durability of a hydride accumulator that provides a constant hydrogen flux.

Conclusions

Experimental study of metal hydrides with metallic and ion-covalent type of bounding is performed. Mathematical models are proposed that describe kinetics of absorption and desorption of hydrogen. Their adequacy is confirmed by comparison with experimental results. Factors having effect upon rates of uptake and release of hydrogen by metal hydrides are analyzed; ways of their optimization are discussed.

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References

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