EXPERIMENTAL STUDY AND MODELING OF THE KINETICS OF DECOMPOSITION of MgH_2

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Introduction

Magnesium hydride is one of the most perspective material for hydrogen storage due to its high hydrogen storage capacity (7.5 wt %). However absorption/desorption rates in magnesium are unsatisfactory for wide industrial application. Improvement of kinetic characteristics can be obtained due to catalyst addition [1], formation of nanocomposites with low temperature hydrides [2], chemical modification using organic materials and graphite-magnesium composites [3] or ball milling [4]. At that it is possible modification of surface or bulk properties of the material or simultaneous modification of both surface and bulk properties.

In the most cases researchers use Avrami equation for modeling of the entire desorption process and for evaluation of kinetic parameters of hydrogen desorption from the magnesium hydride (and/or it's alloys) [5-6]. In our opinion it isn't quite correct approach to this problem. Detail description of separate stages of complicated process of hydrogen desorption from the magnesium hydride is needed.

Experimental details

The magnesium hydride was obtained by direct synthesis from previously mechanically grinded magnesium and hydrogen of high purity (99,999%). Synthesis was carried out at 400-470 C and pressure up to 30 MPa. Product content was controlled by measuring of quantity of absorbed hydrogen and following radiographic analysis. Obtained hydride contained up to 4-5 wt% of metal magnesium. After the synthesis the magnesium hydride was placed into several airproof containers by means of a glove box.

Desorption study was carried out in a high-vacuum device. The range of available pressures was $10^{-5} – 10^{5}$ Pa. For minimization of oxidation the samples (usually 30-40 mg) were extracted from the airproof containers and then placed into the closed autoclave by means of nitrogen atmosphere box. Then the autoclave was mounted to the desorption device and then it was pumped to $10^{-4} – 10^{-5}$ Pa.

Hydrogen desorption from the magnesium hydride was implemented by linear heating of the autoclave containing the hydride powder. Outer nichrome heater was controlled by the computer. For improvement of heat transmission from the walls of the autoclave to the sample gaseous hydrogen (13.33 kPa) was let in a working chamber joint to the autoclave. During the desorption experiment only the autoclave with the inner volume 3-4 ml was heated, whereas in the screened working chamber with the inner volume 315 ml the gas was kept at constant (room) temperature. Hydrogen extraction from the hydride increased the pressure in the working chamber. The pressure was measured by capacitance gauges Varian CeramiCel. During desorption the pressure in the working chamber increased from 13.33 to 20-24 kPa.

The same device was used for the formation of the magnesium hydride at temperature 250°C and hydrogen pressure 100 kPa.

Results and discussion

A series of the desorption curves was obtained at heating rates 0.2, 0.1, 0.05 and 0.025 K/s. Experimental data represents s-like curves of the pressure in the working chamber. But it is more suitable for us to present data as desorption peaks (Fig.1). Repeated experiments revealed good reproducibility of the data.

Two desorption curves obtained at the same heating rate and different initial hydrogen pressure in the working chamber practically coincided. This fact and good reproducibility of the data indicate that: 1) the temperature of the powder during desorption is very close to the temperature of the autoclave due to the filling of the reactor with the hydrogen; 2) used low pressures of the hydrogen don't influence the kinetics of the desorption from the magnesium hydride.

Data processing by means of Avrami equation didn't allow fitting satisfactorily the experimental curve by the model one under any rational values of activation energy and characteristic parameter of the process "nucleation and growth".

We believe that nucleation stage plays the most important role in the process of the hydrogen desorption from MgH_2. Because of low concentration of free electrons compared to the metal an activation barrier E_{hydr} for hydrogen recombination is high. Therefore the desorption flux initially pass-

ing from the hydride surface is very low. However after the nucleus of metal on the hydride surface appears (410-430 C), the desorption is passing from the metal surface with the much higher rate because $E_{met}<E_{hydr}$. In other words the metallic magnesium on the surface of the hydride particles becomes the main channel of the hydrogen desorption. After that the most probable limiting stage is moving of the hydride/α-solution boundary.

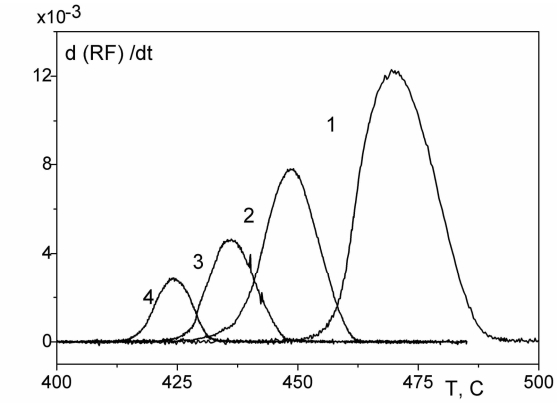

Fig.1. Desorption from MgH_2 at heating rates: 1–0.2, 2–0.1, 3–0.05, 4–0.025 K/s.

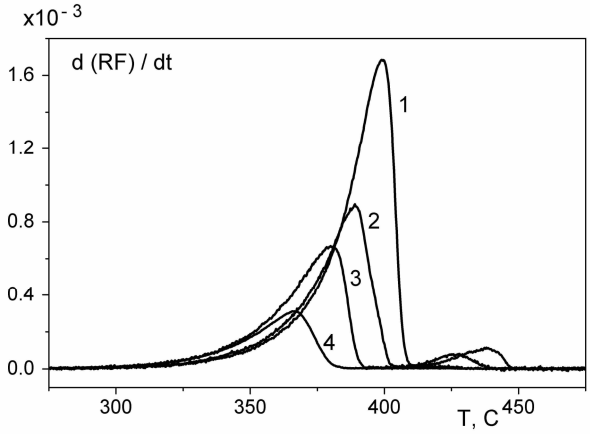

Fig.2. Desorption from partially hydrided magnesium. Heating rate - 0.1 K/s. RF_0: 1–0.43, 2–0.27, 3–0.21, 4–0.10.

We degassed also partially hydrided magnesium. Hydriding was performed in the same working chamber at 100 kPa and 250 C during 12-60 hours. The samples with different reacted fraction (RF_0=0.43, 0.27, 0.21, 0.10) were obtained. Then the samples were degassed using standard methodic. The results are presented in Fig.2. The samples with RF_0= 0.21, 0.10 demonstrate a single desorption peak, whereas the samples with RF_0= 0.43, 0.27 reveal two desorption peaks. The second peak takes place at 425-440°C. We believe that it is associated with the hydrogen desorption from the particles with completely formed hydride skin. The first peak is the desorption from the particles where the hydride skin was not formed completely. Here remarkable hydrogen desorption starts at 330-340 C and finishes at 380-410°C depending on RF_0. A shift of the desorption start to the lower temperature is conditioned namely by the presence of the metal magnesium at the surface of the hydride, since the metal surface presents facilitated channel of the desorption in comparison with the hydride surface.

Conclusions

A series of the curves of the magnesium hydride decomposition is obtained at linear heating in a hydrogen medium. It was revealed that the kinetic curves cannot be satisfactorily fitted on the basis of Avrami equation. A mechanism of desorption is proposed for the cases of formed and non-formed hydride skin.

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