STUDYING OF THERMODYNAMIC AND KINETIC CHARACTERISTICS OF THE HYDROGEN DESORPTION IN MAGNESIUM HYDRIDES

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Introduction

Magnesium hydrides still to be the perspective materials as hydrogen storage alloys, and attract substantial scientific interest. Thermodynamic and kinetic properties of the hydrogen desorption process are the primary characteristics of the hydride materials.

Literature data on the magnesium hydride (β-MgH_2) heat of formation mainly have a range from -72 to -76 $KJ \cdot mol^{-1}$ H_2 [1]. Beside this in [2] the value of $\Delta_f H^0(MgH_2)$ = -91 $KJ \cdot mol^{-1}$ H_2, obtained by full combustion of the hydride in oxygen, is recommended as the most reliable. In the recent works (e.g., [3]) the value -74 $KJ \cdot mol^{-1}$ H_2 also can often be met.

There are no any concerted data for the influence of mechanical treatment of the magnesium hydride on its phase formation thermodynamic and kinetic characteristics in literature for the moment. This is the consequence of the absence of the account for mechanical (energetic) influence on the system Mg — H_2. However, it can be thought established that changing of the hydrogen desorption enthalpy, some decrease in the temperatures at which this process begins, γ-MgH_2 phase formation take place only after some substantial mechanical treatment.

Therefore, the aim of this work was to make more accurate the existent literature data for enthalpy of formation of MgH_2 by studying of hydrogen desorption reverse reaction with the surely approved calorimetric method, and investigations of the phase formation processes in magnesium hydride obtained mechano-chemicaly.

Experimental

MgH_2 specimen was synthesized in a Siverts type device. According to the manometric measurements hydride contains 2.6% mass. H_2. Simultaneous hydrogen analysis was performed with precision method of reduction extraction in helium flux and gas chromatography. Hydrogen content was 2.7% mass. H_2, which allowed to take hydride gross-formulae as $MgH_{0.65}$.

The second specimen was taken by mechanochemical method which consists in milling of magnesium powder in planetary-type mill under hydrogen pressure of 1.2 MPa. Complete attestation of the preparation and the results of volumetric and differential thermal investigations are reported elsewhere [4].

The principal thing was using of calorimetric column of Setaram HT-1500, constructed by the principle of Calve's high-temperature calorimetry, for thermodynamic measurements. Measured quantity in this case isn't the temperature difference ΔT (as in DTA and often DSC devices), but the difference of heat fluxes Δq in the specimen and etalon. The application of such approach allowed distinguishing the maximum error of 1.5-2.0 % when the values of heat effects in dependence on temperature localization are measured. Since for calculation of desorption enthalpy besides Q value one needs to know the quantity of evolved hydrogen, joint use of two approaches gives opportunity to calculate values of $\Delta_{des} H^0(MgH_2)$ with total error not higher than 3 %.

Results and discussions

During the first experiment (Fig.1a) pressed sample of $MgH_{0.65}$ in measuring sell was provocatively placed on to Al_2O_3 backing. Exothermal effect of Mg oxidizing prior to hydrogen desorption peak earnestly reveals the possibility of lowering of endothermic signal. Modern DTA and DSC calorimeters often have measurement sells made from oxide materials, and as a result there is possibility for getting lowered data for $\Delta_{des} H^0(MgH_2)$. Placing the specimen into the tantalum ampoule (Fig.1b) allows reducing oxidation to the minimum level, caused by the existence of the oxygen admixtures in argon.

Calculated value of the hydrogen desorption enthalpy in the former case is $\Delta_{des} H^0(MgH_2)$ = 77,7±2,3 $KJ \cdot mol^{-1}$ H_2. Therefore, the absolute values of $\Delta_{des} H^0(MgH_2)$ and $\Delta_f H^0(MgH_2)$ are lesser than value gotten by us, and can be lowered because of high affinity of magnesium with oxygen.

Obtaining of Mg hydride mechanochemicaly is the reason for substantial changes in hydrogen

excretion character. Oxidation of magnesium matrix takes place only after complete hydrogen discharge (Fig.2b). Beginning of hydrogen excretion is characterized by lower temperature and has the diffusion mechanism. After the main period of desorption (similar to Fig.1) high temperature endothermic effect occurs, followed by oxidation. However, the most important result is in changing of thermodynamic parameters of hydrogen desorption. Thus, desorption enthalpy determined in special experiment in vacuum (Fig. 2a) has value only 58,4 $KJ \cdot mol^{-1}$ H_2. Calculation of $\Delta_{des}H^0(MgH_2)$ of this material in argon has difficulties with complete account of high temperature peak 5 (Fig.2b) and leads to some lowered value of 56,7 $KJ \cdot mol^{-1}$ H_2.

Reducing of the hydrogen desorption enthalpy value for mechanical specimens is an evidence for the partial change in chemical bond character in the Mg-H_2 system.

Fig.2. Hydrogen discharge from MgH_x thermogram after 3 hours treatment: **a** – vacuum, **b** – argon. 1,3,4,5 – des. H_2, 2 – Al_2O_3 drop, 6 – oxid. Mg

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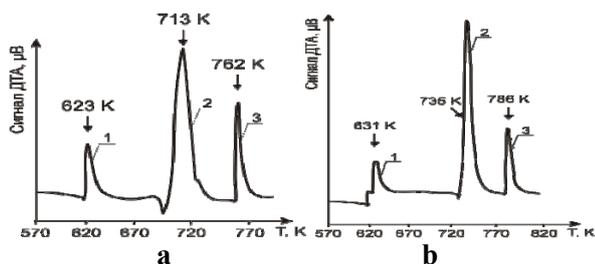
Fig.1. Hydrogen discharge from MgH_2 in argon thermogram: **a** – without ampoule, **b** – in the tantalum ampoule. 1,3 – standard Al_2O_3 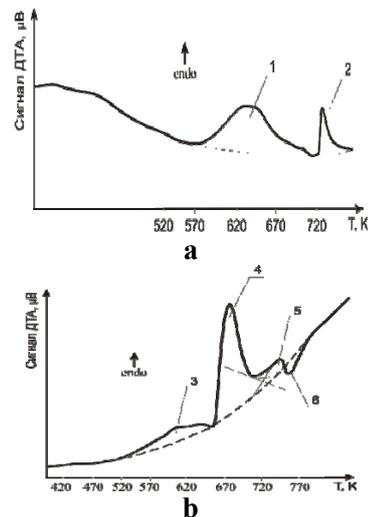drop, 2 – hydrogen desorption from MgH_2.