

TO A QUESTION ABOUT THE TEMPERATURE OF DECOMPOSITION OF THE HYDRIDE PHASE OF MgH_2 , OBTAINED BY THE DIFFERENT METHODS

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In spite of the huge number of studies, dedicated to magnesium hydride, still is absent single-valued answer to a question, which the actual temperature of decomposition in a atmosphere of hydrogen of the stichometric MgH_2 with the standard conditions (i.e. which the temperature of the phase transformation $MgH_2 \rightarrow Mg +$ of $gasH_2$ with the isobaric heating of model in a atmosphere of hydrogen at its normal pressure). Thus, in accordance with the isobaric at the pressure of 1,013 bar with the section of diagram of state Mg - H [1], built according to the experimental data from different sources, the temperature of decomposition of dihydride of magnesium into metallic magnesium and gaseous hydrogen is 561K [2], 575K [3], 590K [4]. At the same time according to the data of isobaric DSK of measurements the decomposition of commercial hydride – MgH_2 , of firm Th. Goldschmidt AG, begins only at a 713K [5] with the peak DSK-curved at a temperature 720K (measurement they were carried out at a pressure of hydrogen of 2bar and rates of heating model 20deg/min). The temperature of decomposition of hydride MgH_2 , obtained by a number of the authors the reactive mechanical fusion (RMS), occurs also substantially higher than obtained by direct hydrogenation from the gas phase in [2-4]. If we compare temperatures of decomposition MgH_2 , which are given to [2] and [5], then let us note their essential difference into 159⁰, in spite of that in both works the thermal desorption of hydrogen from magnesium hydride and its decomposition they observed with the close conditions: at a pressure of hydrogen of 1 bar into [2] and 2 bar - into [5]. Which of the factors made a main contribution to the difference of temperatures of decomposition indicated, given in [2] and [5] - difference in the structural state of studied in these works hydride of magnesium, in the chemical composition and the state of its surface or difference under the methods used and the conditions of investigating the phase transformation $MgH_2 \rightarrow Mg + gasH_2$ and measurement of its temperature? Obtaining answer on this question was the object of study in this work. For this purpose at a normal pressure of hydrogen in the reactor (0,1MPa) and at other

close pressures 0,31MPa, 0,42MPa are investigated the isobars of the desorption- absorption of hydrogen and are determined temperatures of decomposition of dihydride of magnesium, obtained by two different methods: to direct hydrogenations from the gas phase and by reactive mechanical fusion in a atmosphere of hydrogen at a pressure 1,2MPa for 5 hours.

Two isobars ($p= 0,1$ & $0,42MPa$) of the desorption of hydrogen from MgH_2 , obtained by the first method (by hydrogenation from the gas phase, it after which followed endurance in air in the course of the month), were given to fig.1. Curves of desorption obtained on the volumetric installation of original construction, intended for the study by the isobaric method of the processes of the thermal desorption of hydrogen from metals-hydride at its constant pressure in the reactor of in the range 0,1 - 1,0MPa. From that given to fig.1 of curves of desorption with $p=0,1MPa$ and rate of heating 1deg/min. it is evident that the intensive isolation of hydrogen, which testifies about the beginning of the decomposition MgH_2 , begins at a temperature of 443⁰C. This by 155⁰ is higher than the temperature, expected from the data of the work Stampfer [2], which in contrast to our data were obtained in the model of magnesium hydride with the practically free from the oxides (hydroxides) surface (dependence of the decomposition pressure MgH_2 on the temperature in the conditions of three-phase equilibrium was studied into [2] in the model of hydride of magnesium, which after its obtaining from the installation did not take out itself and it was not in the contact with atmospheric air). So high a temperature 443⁰C of the beginning of the decomposition MgH_2 at a pressure of hydrogen in the reactor 0,1MPa serves as indication that in our case on the surface (on the boundaries) of grains of the hydride phase MgH_2 could be formed the oxide (hydroxide) of magnesium practically impenetrable for atomic hydrogen. Such oxide (hydroxide) is capable to hinder the process of the transport of hydrogen atoms from hydride during the gas phase and their association into the molecules and to, as a result, detain the decomposition reaction MgH_2 ; however, only to the specific temperature. We

assume that the temperature of 443⁰C is that temperature, on the reaching by which occurs the restoration of the oxide of magnesium or such transformation, which leads to a sharp increase of atomic hydrogen passage and catalytic activity with respect to the associative desorption of hydrogen.

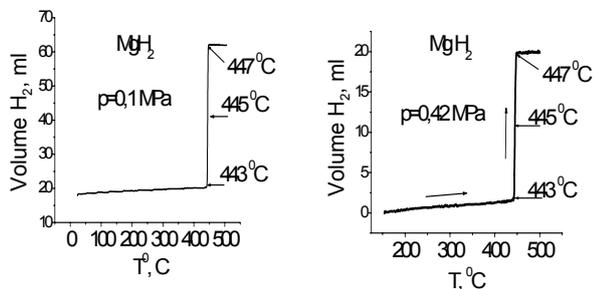


Fig.1

Only afterward this begins at the same temperature of 443⁰C the decomposition MgH₂, that is found at the beginning of reaction in the essentially nonequilibrium state. As confirmation an increase in the pressure in the reactor from 0,1MPa to 0,42MPa did not lead to a change in the temperature of the beginning of the intensive isolation of hydrogen and beginning of the decomposition MgH₂ 443⁰C, (see Fig.1).The isochore of the hydrogen desorption from the obtained hydride MgH₂ is given in Fig.2 and it attests to the fact that with its heating from the room to the 443⁰C the hydrogen desorption practically is absent, above 443⁰ it is observed the intensive isolation of hydrogen and the behavior of our hydride MgH₂ differs little from the behavior of magnesium hydride into [2], if we judge by the value of the equilibrium pressure attainable at its decomposition (more than 40 atm.).

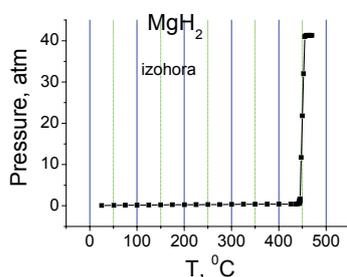


Fig.2.

As can be seen from fig.3, where is the isobar of the desorption of hydrogen at a pressure of 0,1MPa from that obtained by us the reactive mechanical fusion of the hydride phase MgH₂, the temperature of the beginning of the intensive isolation of hydrogen (i.e. the beginning of its decomposition) to 80⁰ is lower than in our MgH₂ of

direct hydrogenation from the gas phase (see Fig.1), but by 75⁰ higher than in MgH₂ Stampfer [2]. The decrease to 80⁰ temperatures of decomposition of the hydride phase MgH₂ is caused, in our opinion, not only by the decrease of particle size in obtained by RMS hydride of magnesium, but also by others the nature of resultant on the surface of such hydride particles (hydro-) oxide (it is borne in mind its sufficient hydrogen-permeability and a reduced temperature of restoration).

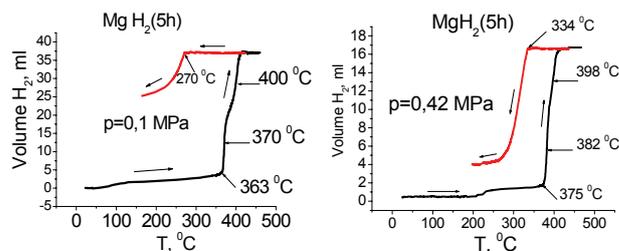


Fig. 3

Here should be focused attention on the fact that on the isobar of the desorption of hydrogen at a pressure in the reactor 0,42 MPa the temperature of decomposition of the hydride phase MgH₂ into 12⁰ is higher than at a pressure 0,1 MPa (see Fig.3).

The carried out analysis has showed that an essential difference in the given values of the temperature of decomposition of the hydride phase of MgH₂ in the different works should be connected, first of all, with the difference under methods and conditions for its obtaining, but not with the varied conditions and methods of thermal analysis and obtaining the curves of the hydrogen desorption by the different authors.

References

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