INFLUENCE OF OXYGEN-STABILIZED η-PHASE ON THE HYDROLYSIS PROPERTIES OF MgH_2

OLEKSANDR KONONIUK

Karpenko Physico-Mechanical Institute of NAS of Ukraine

Magnesium hydride has a high hydrogen capacity, environmental friendliness and low cost. One of its applications is the use of composites based on it in hydrolysis reactions in order to obtain hydrogen and supply it to fuel cells. This report presents an overview of works to show the catalytic effect of oxygen-stabilized η-phases $Zr_3V_3O_{0.6}$, $Ti_{4-x}Fe_{2+x}O_y$, Ti_3Fe_3O and graphite on the mechanochemical synthesis of hydride composites, their sorption-desorption properties and hydrogen generation in the process of hydrolysis reactions in distilled water and in $MgCl_2$ solutions of different concentrations.
Keywords: magnesium hydride, hydrogen generation, hydrolysis.

In recent decades there has been a growing interest in light metal hydrides in the world of which the greatest interest is given to magnesium hydride, which has a hydrogen capacity of 7.6 wt.% and is much cheaper than other metal hydride materials. However, the practical use of magnesium hydride in hydrogen storage systems is limited due to a number of significant disadvantages: high temperatures/pressures (>300°C and 5-10 MPa respectively), low sorption-desorption rates, difficulty of activation, low cyclic stability. Improvement of hydrogen sorption-desorption parameters can be achieved by mechanochemical milling with various catalytic additives.

Another interesting application of magnesium hydride or its composites is their use in hydrolysis reactions to obtain hydrogen and supply it to fuel cells (FC). MgH_2 hydrolysis reactions in water are characterized by a low yield of hydrogen and the process is very slow. To increase the speed and yield of hydrogen, hydrolysis is carried out in solutions of acids or salts [1]. MgH_2 is often synthesized by mechanochemical milling to obtaine a nanostructured hydride with uniform inclusion of catalyst particles, increasing the effective reaction area and concentration of defects. At the same time, it is sense to add such additives as graphite, which prevents agglomeration of particles during milling.

This report will present an overview of the works carried out with the author's participation to show the catalytic effect of oxygen-stabilized η-phases $Zr_3V_3O_{0.6}$, $Ti_{4-x}Fe_{2+x}O_y$, Ti_3Fe_3O on the mechanochemical synthesis of hydride composites, their sorption-desorption properties and hydrogen generation by the hydrolysis reactions. In our recent studies, it was shown that the use of $Zr_3V_3O_{0.6}$ suboxide and C as catalytic additives is an effective way to obtain composites based on MgH_2 with dual applications: for hydrogen storage and for obtaining hydrogen by hydrolysis [2]. Works [3, 4] show the influence of Ti_3Fe_3O and C additions on the hydrogen sorption properties of the corresponding composites and on the hydrogen generation by hydrolysis. For the same purpose, composites with additions of oxygen-stabilized compound $Ti_4Fe_2O_{0.3}$ and graphite were studied.

The starting components for the preparation of hydride composites were two types of magnesium (shavings and high-purity finely dispersed powder), graphite powder, as well as melted in an electric arc furnace and annealed $Zr_3V_3O_{0.6}$, $Ti_4Fe_2O_{0.3}$ and Ti_3Fe_3O alloys. The composites were prepared by reactive ball milling in hydrogen using Fritsch Pulverisette-6 planetary mill. Hydrogen sorption-desorption of the synthesized composites was studied on a Sieverts-type apparatus. The X-ray phase analysis of the samples was performed on a DRON-3.0 powder diffractometer (Cu-Kα radiation) and the data were analyzed by full-profile refinement using the Rietveld method. The kinetics of hydrolysis was studied under pseudoisothermal conditions and the amount of released hydrogen was measured by the volumetric method. Hydrolysis was carried out in deionized water and $MgCl_2$ solutions of different concentrations. At the end of the reaction, a solution of citric acid was added to achieve complete release of hydrogen from the particles that were completely hydrolyzed.

It is shown that the rate of hydrogen absorption depends on the quality and dispersion of the original magnesium. The use of finely dispersed magnesium reduces the time of hydride formation by 5 times compared to shavings. Prolonged ball milling increases the reaction rate and hydrogen yield in hydrolysis reactions. The influence of catalytic additives on the yield of hydrogen in hydrolysis reactions in distilled water in the first 2000 s has the following sequence: $Ti_3Fe_3O > Ti_4Fe_2O_{0.3} > Zr_3V_3O_{0.6}$. When using $MgCl_2$ solution the degree of conversion increases significantly. A strong dependence of the conversion rate on the concentration of $MgCl_2$ was observed. For a concentration of 0.05 mol of $MgCl_2$, the degree of conversion for all composites was in the range of 70-80%. It is shown that the proposed MgH_2 – η-phase – C composites can be used both in hydrogen storage systems and in hydrolysis devices for powering FCs.

1. *Berezovets V., Kytsya A., Verbovytskyy Yu., Zavaliy I., Yartys V.* Hydrolysis of MgH_2 in $MgCl_2$ solutions as an effective way for hydrogen generation // *In book* "Hydrogen based energy storage: status and recent developments. – 2021. – P. 38-52.
2. *Zavaliy I., Berezovets V., Denys R., Kononiuk O., Yartys V.* Hydrogen absorption-desorption properties and hydrolysis performance of MgH_2-$Zr_3V_3O_{0.6}H_x$ and MgH_2-$Zr_3V_3O_{0.6}H_x$-C composites // J. Energy Storage. – 2023. – 65. – P. 107245.
3. *Berezovets V., Kononiuk O., Denys R., Zavalii I.* Synthesis and hydrogen sorption of MgH_2 composites with TiFe and Ti_3Fe_3O additions // Physicochemical mechanics of materials. – 2023. – 2. – P. 73.
4. *Kononiuk O., Zavalii I., Berezovets V., Kytsia A., Borukh I.* Production of hydrogen by hydrolysis of magnesium hydride composites with additions of TiFe/Ti_3Fe_3O and graphite // Physicochemical mechanics of materials – 2023. – 3. – P. 60.