

Hydrogenation of Magnesium in the Presence of ZrV_2

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Abstract—Magnesium is one of the most promising materials for hydrogen storage systems. For a feasible optimization of its hydrogenation conditions, the interaction of mixtures of 200-micron commercial Mg powders with 10–50 wt % of the intermetallic compound ZrV_2 with high-purity hydrogen under a pressure of 3 MPa in the temperature range of 350–390°C was studied. The effect of the activating additive of the intermetallic compound in an amount of 20 wt % on the Mg hydrogenation process was ascertained: at 370–380°C, magnesium is hydrogenated by 95% in a mixture with the hydride of the intermetallic compound and the product contains about 6.4 wt % in total of high-purity hydrogen (99.999 wt %) released at 380–450°C. This mixture is recommended as a working substance in metal hydride hydrogen storage units to release high-active pure hydrogen for laboratory or small-scale works.

Keywords: magnesium, intermetallic compound, hydrogen, hydrogenation, metal hydride hydrogen storage tank

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THEORETICAL ANALYSIS

For the successful development of hydrogen energy technologies, it is necessary to solve the most important problem of efficient, safe and economically advantageous hydrogen storage. Among the various methods and techniques aimed at solving this problem, solid state hydrogen storage in the form of metal hydrides, alloys and intermetallic compounds [1–5] deserves special attention from researchers and technologists.

In terms of gravimetric (7.6 wt %) and volumetric (120 kg/m^3) hydrogen storage capacity magnesium dihydride has the advantage among reversible hydrogen storage materials, but its use in practice encounters difficulties because the hydrogenation of magnesium occurs at high temperatures and is accompanied by a slowdown in the hydrogenation rate over time due to the formation of a MgH_2 layer on the surface of the metal.

Currently, most of the works aiming at the mitigation of magnesium hydrogenation conditions are associated with the use of various catalytic additives [6–17], with achieving nanoscale magnesium particles and scale effect on the parameters of the hydrogenation process [12, 16, 18]. In addition, works are actively pursued in order to find and develop novel hydrogen storage composite materials based on magnesium [6, 10, 12, 14–16, 19], in which submicro- or nanosized magnesium grains are isolated from each other [6, 12, 16].

Among the catalytic additives, the so-called poly-metallic catalysts are of practical interest. These are intermetallic compounds of various structural types ($LaNi_5$ [20], TiFe [13, 21], $TiMn_2$ [21, 22], Mg_2Ni [23–26], Ti_2Ni [21], Al_3Ti [27] etc.), the main purpose of which is to reduce the energy barrier of the dissociation reaction of the hydrogen molecule on the surface of hydrogen storage materials [16, 19].

By thermogravimetric analysis and pressure-composition isotherms measurements, a systematic study of the effect of additives of intermetallic compounds of various structural types (TiAl, Ti_3Al , TiNi, TiFe, TiNb, $TiMn_2$, TiVMn) on the hydrogen sorption and desorption properties of Mg/ MgH_2 has been performed, and a positive effect of titanium-containing intermetallic compounds on the kinetics of the corresponding hydrogenation/dehydrogenation reactions has been established [21].

The intermetallic compound $TiMn_2$ as a possible promising additive for increasing the rate and mitigating the conditions of magnesium hydrogenation in an amount of 10 wt % under high-energy ball milling conditions with Mg under a hydrogen pressure of 70 atm for 50 h formed a composite, which was used for a further study in the form of tablets obtained by the cold pressing method [22]. Such a nanocomposite system of $MgH_2 + 10 \text{ wt } \% TiMn_2$ with a high hydrogenation/dehydrogenation rate at 225°C absorbed/desorbed 5.1 wt % hydrogen under a pressure of 10/0.2 atm for 100 and 400 s, respectively, with

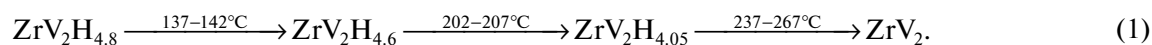
high cyclic stability. The composite was successfully used to obtain a constant hydrogen flow of 150 mL/min (3 A, 5.5 V) in a fuel cell with proton exchange membrane. The observed increase in the hydrogen sorption properties of the system is explained by the synergistic effect of using high-energy ball milling and cold pressing [22], but it is necessary to take into account the highly energy- and technologically expensive methods of preparing the composite when using such a hydrogen storage system in practice.

Thus, the presence of intermetallics has a positive effect on the kinetics of magnesium hydrogenation, but it should be noted that in almost all studies of the reaction of magnesium with hydrogen using catalytic additives of polymetallic phases for the preparation of composites with nanosized particles, long-term high-energy grinding in ball mills under hydrogen atmosphere was applied, which is associated with the use of special equipment and high energy costs.

As a continuation of the work on the use of intermetallic compounds as catalytic additives to mitigate the conditions of magnesium hydrogenation without

the use of preliminary high-energy treatment of the mixture [23] we have studied the hydrogenation of commercial magnesium powder in the presence of the intermetallic compound ZrV_2 , which interacts with hydrogen under conditions acceptable for practical application. ZrV_2 attracts a certain interest among hydride-forming intermetallics due to the ease of its mechanical and chemical processing and the possibility of complete reversible hydrogenation without decomposition of the metal matrix.

According to the data obtained [28] in the system Zr–V there exists one intermetallic compound ZrV_2 with the cubic structural type $MgCu_2$ ($a = 7.439 \text{ \AA}$) forming in the peritectic reaction at 1300°C . The compound ZrV_2 readily interacts with hydrogen under 40 atm at room temperature to produce the hydride with a composition of $ZrV_2H_{4.8}$ ($a = 7.954 \text{ \AA}$ [29]) retaining the crystal structure of the initial metal matrix. The three-stage thermal decomposition of the hydride, according to [30], proceeds according to scheme (1) and ends with the complete release of hydrogen from the hydride phase.



It has also been reported [31, 32] that a hydride phase of ZrV_2 with the composition $ZrV_2H_{4.53}$ was obtained. The phase contains a lower amount of hydrogen (2.29 wt %) and also crystallizes in a cubic syngony with the lattice period $a = 7.913 \text{ \AA}$.

Thus, the aim of the present work is to establish the possibility and determine the optimal conditions for hydrogenation of a mechanical mixture of commercial magnesium and ZrV_2 intermetallic powders without preliminary activation in a ball mill under hydrogen atmosphere for subsequent use as an effective bed material in cyclic-stable metal hydride hydrogen storage tanks serving as sources of highly pure active hydrogen.

EXPERIMENTAL

We used commercial magnesium powder with a particle size of 200 μm and a purity of 99.95 wt %, electrolytic vanadium of the VEL-1 grade with a purity of 99.95 wt %, zirconium with a purity of 99.99 wt %, and high-purity hydrogen (99.9999 wt %) released upon heating a metal hydride hydrogen storage tank based on the $LaNi_5$ intermetallic compound [5].

The intermetallic compound ZrV_2 was obtained by melting a charge of the individual metals in an electric arc furnace with a non-consumable tungsten electrode under a purified argon pressure of 2 atm. The obtained alloys were further annealed in vacuum-sealed quartz ampoules at 800°C for 250 h, followed by quenching in

cold water. X-ray phase analysis ascertained the cubic $MgCu_2$ structural type of the alloys with the crystal lattice parameter $a = 7.441 \text{ \AA}$.

Powders of ZrV_2 were prepared by crushing of an ingot of the alloy in a metal mortar followed by sieving the fraction with a particle size of up to 200 μm .

All operations of samples preparation for both hydrogenation and various types of analysis were carried out in a dry box (MBRAUN) in an atmosphere of high-grade argon with a water and oxygen content of no higher than 0.0001 %.

Samples for the hydrogenation were prepared by mixing the weighed portions of magnesium and intermetallic powders corresponding to a certain quantitative composition of the mixture in a titanium mortar and loaded in a quartz test tube which was placed in a 60-mL reactor autoclave of a metal laboratory high-pressure Sieverts setup.

Before the hydrogenation, 3 g of the powder mixture was outgassed by evacuation (10^{-3} Torr) at $350-390^\circ\text{C}$ for 1 h. Then, the autoclave at the outgassing temperature was filled with hydrogen to a pressure of 30 atm. Hydrogen absorption began without an induction period; the process was continued for 1 h and then heating was stopped.

To determine the duration and completion of hydrogenation processes carried out at different temperatures, a cycling procedure was used. The procedure consists of repeated heating of the autoclave at the synthesis temperature for 2 h with subsequent

Table 1. Conditions and results of hydrogenation of mixtures Mg + ZrV₂

Sample no.	Composition of Mg : ZrV ₂ , wt %	Hydrogenation conditions		Hydrogen content in the hydrogenation products, wt %	
		T, °C	τ, h	observed	calculated*
1	90 : 10	380	9	6.58	7.08
2	90 : 10	370	9	6.66	7.08
3	90 : 10	360	9	6.37	7.08
4	80 : 20	390	5	6.18	6.57
5	80 : 20	380	5	6.31	6.57
6	80 : 20	370	5	6.37	6.57
7	80 : 20	360	7	6.18	6.57
8	80 : 20	350	9	6.18	6.57
9	70 : 30	370	5	5.74	6.05
10	60 : 40	370	5	5.25	5.53
11	50 : 50	370	5	4.72	5.02

* Under the assumption of 100% hydrogenation.

cooling to room temperature. In the cycling processes, when the mixture is heated, there is a gradual release of active hydrogen from the intermetallic hydride phase, which facilitates the onset of the hydrogenation of the magnesium. This process “vanishes away” over time, but is repeated with the beginning of a new cycle.

After the last cycle completion determined by the cessation of pressure drop in the system, the product was unloaded in the dry box and analyzed.

The hydrogen content of the hydrogenation products was determined by the volumetric method and by chemical analysis carried out on a Vario Micro cube (Elementar GmbH) CHNS/O element analyzer.

The phase composition of the hydrogenated samples was studied by X-ray phase analysis carried out on a DRON-UM-2 automatic powder diffractometer at room temperature ($\text{CuK}\alpha$ radiation $2\theta = 10^\circ - 100^\circ$).

The thermal stability of the reaction products was studied using an STA 409 Luxx synchronous analysis unit from Netzsch. The weight loss (TG) curves were measured and differential scanning calorimetry (DSC) was carried out under temperature-programmed heating at a rate of 10 K/min in an argon flow.

Hydrogen pressure was measured with a standard MO pressure gauge of accuracy class 0.4.

RESULTS AND DISCUSSION

The experiment showed that immediately after the end of degassing, hydrogenation of the mixture for 1 h with subsequent cooling of the autoclave to room temperature is accompanied by the formation of an intermetallic hydride of the composition $\text{ZrV}_2\text{H}_{4.8}$. In this case, magnesium is practically not hydrogenated,

which explains the need for further heating of the reaction mixture in a cyclic mode.

The interaction of mixtures (90–50 wt %) Mg + (10–50 wt %) ZrV₂ with hydrogen was studied in a temperature range of 350–390°C and under a hydrogen pressure of 30 atm, i. e. we studied the possibility and determined the conditions for hydrogenation of magnesium in the presence of 50–10 wt % ZrV₂ intermetallic compound. The results obtained are presented in Table 1.

The selected upper temperature limit of the synthesis (390–380°C) and hydrogen pressure of 3 MPa best correspond to the conditions for obtaining magnesium dihydride. However, at 380°C and the composition of the initial mixture of 90 : 10 wt %, hydrogenation is accompanied by partial decomposition of the hydrides of both the metal and the intermetallic compound formed at the initial stages of the reaction (sample 1), which leads to a low total hydrogen content in the product (6.58 wt %), i.e. 93% hydrogenation, after 8 h of the reaction. Decreasing the reaction temperature to 370°C slightly increased the total hydrogen content in the reaction product to 6.66 wt % (sample 2), and decreasing the temperature to 360°C was accompanied by a decrease in the total hydrogen content in the product to 6.37 wt % (90% hydrogenation) (sample 3), which is probably due to the insufficient duration of the process. Thus, the possibility of hydrogenation of a mechanical mixture of coarse-crystalline powders of commercial magnesium and the intermetallic compound ZrV₂ without preliminary activation in a ball mill in a hydrogen atmosphere has been established.

Further studies aimed at determining the effect of increasing the amount of intermetallic compound in the mixture, the duration of hydrogenation and the temperature regime on the final result of the process,

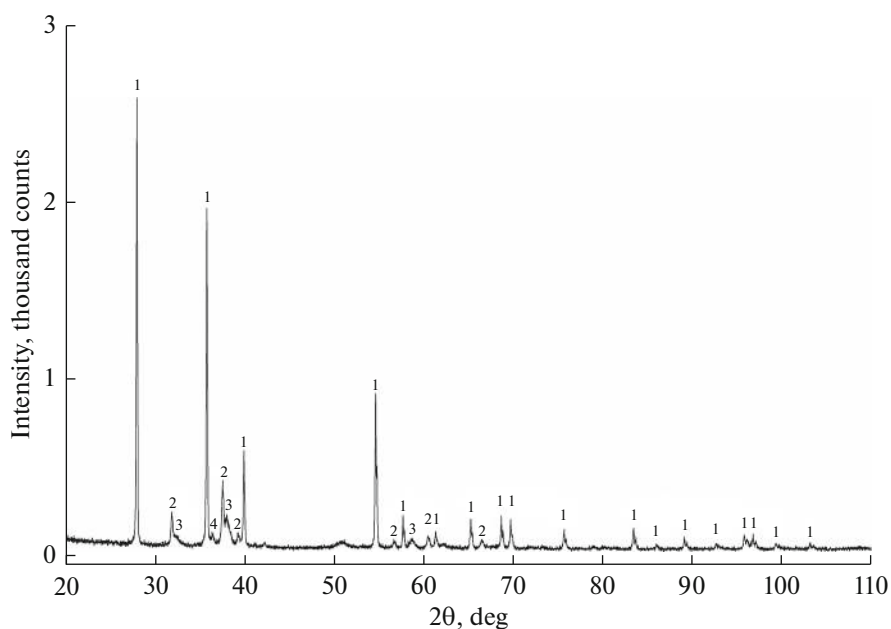


Fig. 1. X-ray diffraction pattern of the product of powder mixture 80 wt % Mg + 20 wt % ZrV₂ hydrogenation at 370°C.

i.e., to optimize conditions for maximum hydrogenation of magnesium in the presence of the intermetallic compound ZrV₂.

Using the example of the reaction of a mixture of the composition 80 : 20 wt % with hydrogen (samples 4–8), the effect of temperature on the completeness of the conversion of the components into a mixture of hydrides was studied. It was found that with a five-hour process duration (samples 4–6), the best result was obtained at a temperature of 370°C: the mixture was hydrogenated by 97 wt % with a total hydrogen content in the mixture of 6.37 wt % (sample 6). At higher temperatures, 390 and 380°C (samples 4 and 5, respectively), the completeness of hydrogenation decreased to 94–95%, which, as indicated above, is associated with the decomposition of hydrides. Hydrogenation of a mixture of the same composition, but at lower temperatures (360 and 350°C) and with an increase in the duration of the reaction (7–9 h, respectively) occurs with a 94% conversion of magnesium into its hydride and with a corresponding decrease in the total hydrogen content in the reaction products to 6.18 wt % (samples 7–8).

An increase in the amount of intermetallic compound in the initial mixture to 30–50 wt % (samples 9–11) during five-hour hydrogenation and a temperature of 370°C is accompanied by a decrease in the total hydrogen content in the mixture due to an increase in the amount of ZrV₂ and an almost identical percentage of magnesium conversion into hydride (94–95 wt %), which is probably due to the insufficient duration of the process. An increase in the hydrogenation time to

9 h (using sample 11 as an example) increased the completeness of hydrogenation only to 96 wt %.

The phase composition of the hydrogenation products is confirmed by X-ray diffraction and differential thermal analysis. As an example, Fig. 1 shows the diffraction pattern of a sample obtained by hydrogenation of a powder mixture of 80 : 20 wt % at 370°C (sample 6). The diffraction pattern shows peaks of magnesium hydride as the main phase (1), the intermetallic hydride is present in two forms with different crystallographic modifications of the metal sublattice: cubic (2—narrow peaks) and tetragonal distorted (3—broadened peaks), unreacted magnesium appears in trace amounts (4).

Figure 2 shows the thermogram of the hydrogenation products of a mixture of 80 : 20 wt % at 360°C: the endothermic peaks at 377 and 442°C correspond to the decomposition temperatures of ZrV₂H₋₅ and MgH₂, respectively (sample 7).

Thus, the addition of 20 wt % ZrV₂ is quite sufficient for almost complete hydrogenation of magnesium at 370°C in 5 h, the total hydrogen content reaches 6.37 wt %.

In the system under study, a hydrogenation mechanism is possible based on the existence of catalytic centers on the surface of the intermetallic phase, which are V and Zr atoms and which participate in the dissociation of H₂ molecules into H atoms diffusing to the magnesium phase through the ZrV₂/Mg boundary, that is, the ZrV₂ phase plays the role of hydrogen transport channel.

The found capability of a mixture of commercial magnesium with the intermetallic compound ZrV₂ to

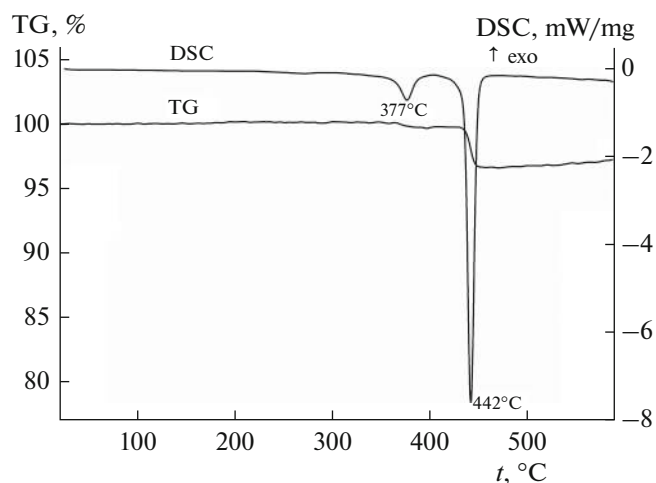


Fig. 2. Thermograms of the product of powder mixture 80 wt % Mg + 20 wt % ZrV₂ hydrogenation at 360°C.

absorb hydrogen at 370–380°C with the formation of hydrides containing 6.3–6.7 wt % hydrogen and releasing it at temperatures up to 450°C was used in high-temperature metal hydride cyclic-stable hydrogen storage units.

We carried out 10 full hydrogenation-dehydrogenation cycles of a mixture of 80 wt % Mg + 20 wt % ZrV₂, the half-cycles of hydrogenation and dehydrogenations were performed at 380 and 450°C, respectively (sample 5). After the 10th cycle, chemical and X-ray phase analyses showed that the products were identical to the initial mixture, i.e. the intermetallic compound did not undergo degradation or oxidation during cycling, and retained its crystalline structure. Such hydrogen storage tanks based on a mixture of MgH₂ + ZrV₂H_{4.53} with external heating are used at temperatures up to 450°C in laboratory or small-scale operations involving highly active hydrogen of high purity (99.999 wt %), they are comparatively cheap and easy to handle. The advantages of the bed material include the possibility of using commercial magnesium powder, the availability of metal components of the intermetallic compound ZrV₂, ease of its preparation, and the absence of preliminary energy-intensive treatment of the mixture.

CONCLUSIONS

A mixture of magnesium and the intermetallic compound ZrV₂, containing up to 6.7 wt % hydrogen after hydrogenation and releasing it at 380–450°C, can be recommended as a bed material for metal hydride cyclic-stable hydrogen storage units as sources of high-purity (99.999 wt %) hydrogen when conducting laboratory or small-scale works.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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