ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2018, Vol. 63, No. 12, pp. 1605–1609. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © V.N. Fokin, E.E. Fokina, B.P. Tarasov, 2018, published in Zhurnal Neorganicheskoi Khimii, 2018, Vol. 63, No. 12, pp. 1589–1594.

PHYSICAL METHODS OF INVESTIGATION

Hydrogenation of a Magnesium–Mg_2Yb Alloy

V. N. Fokin[a, *], **E. E. Fokina**[a], **and B. P. Tarasov**[a]

[a] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia*

**e-mail: fvn@icp.ac.ru*

Received October 10, 2017

Abstract—A possibility for hydrogenation of a two-phase magnesium alloy containing intermetallic compound Mg_2Yb by hydrogen and ammonia is found to yield hydride phases MgH_2 and $MgYbH_{3.5}$ in various temperature schedules. The use of ammonia in the range 350–500°C leads to the formation of magnesium and ytterbium nitrides.

Keywords: hydrogen, ammonia, alloy, intermetallic compound, hydride, nitride, phase transformations

DOI: 10.1134/S0036023618120082

THEORY

An extensive development of research into the reactions of metals, intermetallic compounds, and alloys with hydrogen is due both to demand for expanding and deepening of fundamental knowledge in the chemistry of metals and hydrides and to broad prospects for application of metal hydrides and polymetal phases.

One application field of metal hydride phases is in reversible accumulation of hydrogen as a method for hydrogen storage in a bound state. In this context, magnesium hydride MgH_2 deserves much attention in view of its high weight density, a high hydrogen content, room-temperature synthesis, and other merits [1–4]. However, there are factors that hamper magnesium metal hydrogenation: a high activation temperature, formation of a magnesium hydride layer on the metal surface to inhibit hydrogen penetration, and some others. Various procedures and methods exist for eliminating or suppressing these factors, including mechanochemical treatment [5], metal [6, 7] and organic [8, 9] catalysts, and magnesium hydrogenation in its alloys with an intermetallic compound [10, 11]. One more way is to use ammonia as the hydrogen source in hydrogenation processes [12–14]. With ammonia, hydride phases are frequently formed under milder conditions than by direct hydrogenation [15, 16].

Several methods can simultaneously be used for a mild synthesis of magnesium hydride for search for new magnesium-containing polymetal phases as efficient reversible hydrogen storages. In this context, of interest are two-component magnesium alloys with magnesium-containing intermetallic compounds. The possibility to hydride two-component alloy $Mg_{89}Ni_{11}$ by hydrogen and ammonia was elucidated [14]. It was shown that with the use of ammonia, MgH_2 is formed at a far lower temperature than in the reaction with hydrogen: at 200 against 350°C. The second eutectic alloy component (intermetallic compound Mg_2Ni) is hydrogenated by either hydrogen or ammonia to tetrahydride Mg_2NiH_4. Another magnesium-rich two-phase alloy is $Mg_{80}Yb_{20}$ (hereafter referred to as "two-phase alloy Mg_4Yb"), which is comprised of Mg and Mg_2Yb phases.

The Mg–Yb system is known to form only one intermetallic compound, namely, Mg_2Yb, which melts congruently at 718°C [17]; the solubility of ytterbium in magnesium is 0.05 at % at 200°C. This compound has a great homogeneity extent (29.3–36.2 at % Yb), is a Laves phase, and has a hexagonal structure ($MgZn_2$ structural type: $a = 6.246(1)$ Å, $c = 10.134(3)$ Å [18] or $a = 6.2551(6)$ Å, $c = 10.120(1)$ Å [19]).

There have been only few studies into alloys of the Mg–Yb systems [19–23]; these studies are concerned with the metal solubility in each other [20], solid solutions [22], and liquid alloys [21]. Ebner and Range [19] performed direct high-temperature synthesis of Mg_2Yb from the constituent elements under a high pressure, prepared single crystals, and preformed the complete structural analysis of the intermetallic compound.

Klyamkin et al. [18] in their studies into the reactions of intermetallic compound Mg_2Yb with hydrogen elucidated the existence of a hydride phase of composition $MgYbH_{3.5}$. Mg_2Yb starts to hydride at temperatures above 300°C, and its hydrogenation is accompanied by complete hydrogenolysis to yield a mixture of magnesium and ytterbium dihydrides as probed by X-ray powder diffraction. Dehydrogenation of this mixture at 300–320°C under a residual pressure of 1 Pa gives rise to the complete decomposition of magnesium dihydride, but ytterbium dihydride survives. Multiple hydrogenation-dehydrogenation cycling was found to yield $MgYbH_{3.5}$ (hexagonal crystal system; $a = 6.2718(8)$ Å, $c = 6.8385(13)$ Å). The composition of this phase is verified by desorption isotherms; the hydride phase is isostructural to $MgCaH_{3.72}$ [18].

In this work, we study a possibility to hydrogenate magnesium-rich two-phase alloy Mg_4Yb by hydrogen and ammonia under mild conditions in order to obtain a hydride phase with a high reversible hydrogen content.

EXPERIMENTAL

Magnesium (99.95% pure) and ytterbium (99.9% pure) were used to prepare Mg_4Yb alloy samples. The metal batch encapsulated by a LiCl–KCl eutectic melt was alloyed in a vacuum induction furnace. The composition of the alloy was monitored by chemical analysis and X-ray powder diffraction. Immediately before an experiment, the alloy was cleaned from the surface oxide film, washed with ethanol and diethyl ether, mechanically micronized under argon, and powder particles with sizes below 200 μn were sieved off. The specific surface area (S_{sp}) of this powder was 0.09 m^2/g.

The hydriding agent was high-purity (99.999%) hydrogen, which was evolved upon heating from a metal hydride accumulator based on intermetallic compound $LaNi_5$.

Ammonium chloride (a chemically pure reagent) was dried by degassing for 9 h at 150°C. The ammonia dried by metallic sodium was 99.99% pure.

Hydrogenation and hydronitriding (ammonia treatment of metal phases) of the alloy were carried out in a stainless steel container placed inside an autoclave-reactor of a 60-mL high-pressure setup.

Prior to hydrogenation with hydrogen, an alloy sample (2–3 g) was pre-degassed by heating in vacuo (at ~1 Pa) at 350 or 450°C for 1 h, and hydrogen was admitted to the autoclave at the same temperature under 3.0–3.5 MPa. After hydrogenation was over, the autoclave with the sample inside was exposed to room temperature for several hours for equilibration.

The reaction of alloy powders with ammonia was studied at the initial ammonia pressure of 0.7–0.8 MPa using NH_4Cl (10 wt % of the intermetallic compound) as a process activator. A weight of the prepared powder mixture (0.8–1.0 g) was degassed to ~1 Pa for 30 min at room temperature, ammonia was admitted to the reactor, and the reactor was left to stand for 30 min. Then, the reactor was heated to the set temperature, exposed for 3 h, cooled to room temperature, and again heated. Since the pressure in the system increased in the course of the reaction (up to 1.5 MPa), the end of the process was determined as the cease of pressure change. After several heating–cooling cycles were carried out, the gas phase was released into the buffer tank, the reaction products were discharged under an inert atmosphere and analyzed.

The NH_4Cl was removed from the reaction products via the treatment them by absolute ethanol under stirring for 1 h at room temperature (the procedure was repeated twice).

X-ray powder diffraction experiments were carried out on an ADP-1 diffractometer (CuK_α radiation). The error in unit cell parameters did not exceed 0.005 Å.

The thermal stability of reaction products was studied on an STA 409 Luxx (Netzsch) TG–DTA/DSC simultaneous thermal analyzer under argon (the heating rate was 10 K/min).

The specific surface areas (S_{sp}) of samples were derived from low-temperature krypton adsorption after volatile products were removed from the solid in vacuo (1.3×10^{-3} Pa) at 300°C for 5 h and were calculated by the Brunauer–Emmett–Teller. The determination error was ±10%.

The compositions of the formed phases were determined by volumetric and chemical analyses. The hydrogen and nitrogen were determined on a CHNS/O Vario Micro cube Elementar elemental analyzer. The chlorine was determined by a turbodimetric method.

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

RESULTS AND DISCUSSION

The alloyed sample is two-phase as probed by X-ray powder diffraction. The X-ray diffraction pattern features reflections from Mg_2Yb and Mg phases with the unit cell parameters $a = 6.2549$ Å, $c = 10.125$ Å and $a = 3.2090$ Å, $c = 5.2108$ Å, respectively.

Conditions and results of hydrogenation of alloy with hydrogen are listed in Table 1. After an alloy powder sample was degassed for 1 h and then hydrogenated in a hydrogen atmosphere with the initial pressure of 3.5 MPa for one and a half months, the hydrogen content of the product was 1.2 wt % (Table 1, sample 1); according to X-ray powder diffraction data and with reference to [18], this value evidences the formation of a intermetallide MgYb-based hydride phase of composition $MgYbH_{3.5}$ ($a = 6.2720$ Å, $c = 6.8346$ Å) via the hydrogenolysis of the intermetallic compound Mg_2Yb in the course of hydrogenation. Despite the fact that the hydride phase $MgYbH_{3.5}$ contains 1.74 wt % hydrogen, the aforementioned lower content (1.2 wt %) is due to the fact that metallic magnesium does not take-up hydrogen under these hydrogenation conditions. $MgYbH_{3.5}$ decomposes in one step at 510°C as probed by DTA.

Degassing of the initial alloy at 350°C with subsequent hydrogenation at 200°C for 18 h with the initial

Table 1. Conditions and results of hydrogenation of alloy Mg_4Yb

Sample no.	Degassing parameters		Parameters of synthesis			Reaction products			
						phase composition	unit cell parameters, Å		H, wt %
	T, °C	τ, h	T, °C	p_{H_2}, MPa	τ_{synth}		a	c	
1	~20	1	~20	3.5	1.5 months	$MgYbH_{3.5}$ Mg	6.2720 3.2090	6.8346 5.2118	1.2
2	350	1	350	3.0	12 h	$MgYbH_{3.5}$ MgH_2	6.2724 4.5140	6.8365 3.0200	3.4

hydrogen pressure of 3 MPa does not change the composition of the product mixture. With the same degassing conditions, however, at a higher hydrogenation temperature (350°C) a six fold repetition of heating–cooling cycle gives rise to hydrogenation of magnesium to dihydride MgH_2 ($a = 4.5140$ Å, $c = 3.0200$ Å) (Table 1, sample 2). The hydrogen content of the sample is 3.4 wt % as determined by chemical analysis. When the hydrogenation temperature rises to 400–450°C, the products feature ytterbium dihydride YbH_2 ($a = 5.251$ Å), along with MgH_2 and $MgYbH_{3.5}$, likely due to the hydrogenolysis of $MgYbH_{3.5}$.

As mentioned above, in some cases the use of ammonia instead of hydrogen as the hydriding agent in the presence of the promoter NH_4Cl (in the absence of which hydronitriding does not occur) makes it possible to accomplish formation of hydride phases under milder conditions.

The activation effect of ammonium chloride is due to its reversible decomposition to ammonia and hydrogen chloride at increased temperature. The hydrogen chloride is likely to react with surface metal atoms to yield chlorides, thereby facilitating metal hydrogenation. Since reversible dissociation and recombination of gases under an ammonia atmosphere are very rapid, metal chlorides are formed in insignificant amounts and are undetectable by X-ray powder diffraction.

Table 2 lists the parameters and results of hydronitriding of the studied alloy in the temperature range 100–500°C. The run duration was 28 h. The data compiled in Table 2 show a noticeable effect of temperature on the product composition.

The treatment of the alloy by ammonia at 100°C (Table 2, sample 1) induces the hydrogenolysis of the intermetallic compound of the alloy, so the hydride phase of composition $MgYbH_{3.5}$ ($a = 6.2693$ Å, $c = 6.8371$ Å) is formed. Noteworthy, the hydrogen concentration in the reactor at such a low temperature is several percent; that is, the disproportionation of Mg_2Yb occurs under conditions of so-called mild synthesis. Thus, the hydrogenation parameters (room temperature and high pressure) with hydrogen are almost compensated for by the hydronitriding parameters (weak heating and low pressure) while yielding the same products. Metallic magnesium is almost not hydronitrided at this temperature, just as expected. Hydronitriding is accompanied by pounding of metallic phases; a considerable (up to 24 m^2/g) increase in the specific surface area of the powders signifies the fine-dispersed state of reaction products.

As the hydronitriding temperature rises to 150°C (Table 2, sample 2), magnesium reacts with ammonia as evidenced by the appearance of amide $Mg(NH_2)_2$ ($a = 10.37$ Å, $c = 20.15$ Å) in the reaction products. Apart from the amide, magnesium and hydride phase $MgYbH_{3.5}$ were found in hydronitriding products. Noteworthy, all products of reactions of the alloy with ammonia at temperatures in the range 100–500°C contain this hydride phase; this observation indicates the stability of this phase under these conditions, that is, this phase does not evolve hydrogen up to 500°C.

The hydronitriding products obtained at 200°C (Table 2, sample 3) differ appreciably from the preceding ones; along with $MgYbH_{3.5}$, they contain MgH_2 ($a = 4.5168$ Å, $c = 3.0190$ Å), which is formed by the direct hydrogenation reaction; nitride magnesium Mg_3N_2 ($a = 9.9620$ Å) as the decomposition product of magnesium amide; and trace amounts of the latter. The products formed at 200°C are highly dispersed; their specific surface area is 104.0 m^2/g.

A further 50°C rise in hydronitriding temperature (Table 2, sample 4) enhances the final decomposition of magnesium amide; it is no more detected in the reaction products. As to the other components, the product composition remains unchanged. A similar composition is also typical of the product mixture obtained at 300°C (Table 2, sample 5).

According to DTA data, the reaction products obtained at 250 and 300°C (Table 2, samples 4 and 5) evolve hydrogen in two stages with two endotherms at 440 and 510°C. At the first stage, about 65% of the total hydrogen is evolved from a sample due to the decomposition of magnesium dihydride. At the second stage (at 510°C), hydrogen is eliminated from the hydride phase $MgYbH_{3.5}$.

Hydronitriding at 350°C (Table 2, sample 6) changes the general trend of the reactions. Magnesium hydride appears in the products only in trace amounts,

Table 2. Conditions and results of hydronitriding of alloy Mg_4Yb

Sample no.	Parameters of synthesis		Reaction products				
	T, °C	p_{NH_3}, MPa	*H*, wt %	phase composition	unit cell parameters, Å		S_{sp}, m^2/g
					a	*c*	
1	100	7.9	1.2	Mg $MgYbH_{3.5}$	3.2090 6.2693	5.2118 6.8371	24.0
2	150	8.0	2.1	Mg $Mg(NH_2)_2$ $MgYbH_{3.5}$	3.2089 10.37 6.2690	5.2100 20.15 6.8272	62.4
3	200	7.4	3.3	MgH_2 Mg_3N_2 $MgYbH_{3.5}$ $Mg(NH_2)_2$*	4.5168 9.9620 6.2695	3.0190 – 6.8262	104.0
4	250	7.0	3.4	MgH_2 Mg_3N_2 $MgYbH_{3.5}$	4.5170 9.9647 6.2684	3.0190 – 6.8283	67.6
5	300	8.6	3.2	MgH_2 Mg_3N_2 $MgYbH_{3.5}$	4.5168 9.9637 6.2666	3.0203 – 6.8277	38.1
6	350	8.4	2.4	YbH_2 Mg_3N_2 YbN $MgYbH_{3.5}$ MgH_2*	5.2500 9.9627 4.7792 6.2714	– – – 6.8231	84.8
7	400	8.2	1.8	Mg_3N_2 YbN $MgYbH_{3.5}$ YbH_2*	9.9628 4.7803 6.2704	– – 6.8354	93.0
8	450	8.4	1.7	YbN Mg_3N_2 $MgYbH_{3.5}$ YbH_2*	4.7852 9.9650 6.2713	– – 6.8368	80.9
9	500	7.5		Mg_3N_2 YbN $MgYbH_{3.5}$*	9.9649 4.7861	– –	18.6

* Trace amounts.

but its decomposition in the presence of ammonia yields the corresponding nitride Mg_3N_2. In addition, ytterbium hydride appears in the products, and YbN appears due to its yet small decomposition. The appearance of ytterbium compounds is due to the onset decomposition of the hydride phase $MgYbH_{3.5}$.

Hydronitriding carried out at temperatures in the range 400–500°C (Table 2, samples 7–9) involves the final decomposition of the hydride phase $MgYbH_{3.5}$; in the products obtained at 500°C, this phase is present only in trace amounts. Magnesium hydride is not detected in the hydronitriding products, while magnesium nitride is piled up. The same occurs with ytterbium hydride; it appears in trace amounts at 400–450°C and is absent in the products obtained at 500°C (Table 2, sample 9), ytterbium nitride being a second hydronitriding product at 500°C.

The specific surface area of hydronitriding products rises, as the reaction temperature increases, from 24.0 m^2/g (at 100°C) to 104.0 m^2/g (at 200°C). The subsequently observed considerable scatter in S_{sp} (Table 2) can be associated both with the effect of product composition and with possible sintering at high temperatures, the latter appreciably decreasing the measured powder surface areas. However, the high S_{sp} values (especially for the product of sample 3: 104 m^2/g) indicate the high dispersion of the as-prepared powders. So, in order for these powders to be used as a working material for hydrogen accumulators, high-quality filters should be used in design of the system to prevent the entrainment of powder particles [24].

The unit cell parameters of the prepared compounds listed in Tables 1 and 2 agree with the values known from the related literature.

In summary, our study of hydrogenation of magnesium-rich two-phase alloy Mg_4Yb by hydrogen and ammonia elucidated the formation of hydride phases MgH_2 and $MgYbH_{3.5}$ under relatively mild conditions (200–300°C).

ACKNOWLEDGMENTS

This work is performed within state task no. 0089-2014-0030 and with assistance of the Russian Foundation for Basic Research (project no. 16-29-06197-ofi-M).

REFERENCES

1. T. Sadhasivam, H.-T. Kim, S.-H. Jung, et al., Renev. Sustain. En. Rev. **72**, 523 (2017). doi 10.1016/j.rser.2017.01.107
2. J.-C. Crivello, R. V. Denys, M. Dornheim, et al., Appl. Phys. A **122**, 85 (2016). doi 10.1007/s00339-016-9601-1
3. B. Sakintuna, F. Lamari-Darkrim, and M. Hirscher, Int. J. Hydrogen En. **32**, 1121 (2007). doi 10.1016/j.ijhydene.2006.11.022
4. B. P. Tarasov, M. V. Lototskii, and V. A. Yartys', Russ. J. Gen. Chem. **77**, 694 (2007). doi 10.1134/S1070363207040329
5. S. N. Klyamkin, Russ. J. Gen. Chem. **77**, 712 (2007). doi 10.1134/S1070363207040330
6. H. Yu, S. Bennici, and A. Auroux, Int. J. Hydrogen En. **39**, 11633 (2014). doi 10.1016/j.ijhydene.2014.05.069
7. M. Williams, J. Sibanyoni, M. Lototskyy, and B. Pollet, J. Alloys Compd. **580**, S144 (2013). doi 10.1016/j.jallcom.2013.01.086
8. R. V. Lukashev, S. N. Klyamkin, and B. P. Tarasov, Inorg. Mater. **42**, 726 (2006). doi 10.1134/S0020168506070077
9. Y. Wang, L. Jiao, H. Yuan, and G. Liu, ACS Appl. Mater. Interfaces **6**, 11038 (2014). 10.1021/am502755s
10. P. V. Fursikov, D. N. Borisov, and B. P. Tarasov, Russ. Chem. Bull. **60**, 1848 (2011). doi 10.1007/s11172-011-0279-4
11. R. R. Shahi, A. Bhataganar, S. K. Pandey, et al., Int. J. Hydrogen En. **40**, 11506 (2015). doi 10.1016/j.ijhydene.2015.03.162
12. B. P. Tarasov, V. N. Fokin, E. E. Fokina, and V. A. Yartys, J. Alloys Compd. **645**, S261 (2015). doi 10.1016/j.jallcom.2015.01.007
13. B. P. Tarasov, E. E. Fokina, and V. N. Fokin, Russ. Chem. Bull. **65**, 1887 (2016). doi 10.1007/s11172-016-1529-2
14. V. N. Fokin, E. E. Fokina, S. A. Mozhzhukhin, and B. P. Tarasov, Al'tern. En. Ekol., Nos. 9–10, 58 (2016). doi 10.15518/isjaee.2016.09-010.058-065
15. B. P. Tarasov, E. E. Fokina, and V. N. Fokin, Russ. Chem. Bull. **60**, 1252 (2011). doi 10.1007/s11172-011-0193-9
16. B. P. Tarasov, E. E. Fokina, and V. N. Fokin, Russ. J. Gen. Chem. **84**, 194 (2014). doi 10.1134/S1070363214020054
17. *Phase Diagrams of Binary Metal Systems: A Handbook*, Ed. by N. P. Lyakishev (Mashinostroenie, Moscow, 2001), Vol. 3 [in Russian].
18. S. N. Klyamkin, N. V. Kandalova, V. N. Verbetskii, and K. N. Semenenko, Zh. Neorg. Khim. **36**, 215 (1991) [in Russian].
19. M. A. Ebner and K.-J. Range, J. Alloys Compd. **236**, 50 (1996).
20. Z. Tian, X. Qin, W. Sun, et al., Perspekt. Mater., No. 13, 726 (2011) [in Russian].
21. R. Agarwal, H. Feufel, and F. Sommer, J. Alloys Compd. **217**, 59 (1995).
22. A. V. Dobromyslov, L. I. Kaigorodova, V. D. Sukhanov, and T. V. Dobatkina, Phys. Metals and Metallography, **103**, 64 (2007). doi 10.1134/S0031918X07010085
23. C. Guo and Z. Du, J. Alloys Compd. **422**, 102 (2006). doi 10.1016/j.jallcom.2005.11.060
24. B. P. Tarasov, in *Hydrogen Energy Technologies: Collected Works* (OIVT RAN, Moscow, 2017) [in Russian].

Translated by O. Fedorova