Journal of Alloys and Compounds 509S (2011) S671–S674

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Kinetics of dehydrogenation of MgH_2 and AlH_3

I. Gabis*, M. Dobrotvorskiy, E. Evard, A. Voyt

Physics Department of St. Petersburg State University, St. Petersburg, Russia

ARTICLE INFO

Article history:
Received 11 August 2010
Received in revised form
10 December 2010
Accepted 10 December 2010
Available online 21 December 2010

Keywords:
Metal hydrides
Electronic band structure
Kinetics
Phase transitions
Thermal analysis
Gas–solid reactions

ABSTRACT

Kinetics of dehydrogenation was studied using isothermal barometry, TDS and SEM methods. Two stages of the decomposition process are considered: incubation preceding the formation of metallic nuclei on the surface of the particle and hydrogen evolution via these metallic regions serving as facilitating channels for desorption. Duration of the first stage depends on the temperature of the sample. Relationship with material's electronic band structure is discussed. Kinetics of the second stage is controlled by two reactions: desorption of the hydrogen molecules from the surface and shift of the metal-hydride interphase in the bulk. Physical mechanisms of decomposition with detailed reaction kinetics are proposed and kinetic parameters are evaluated.

1. Introduction

Hydrides of aluminium and magnesium are under close scrutiny of researchers due to their high mass content of hydrogen. An extensive bibliography on magnesium hydride can be found in review [1]. Recent studies of alane are presented in works [2–5]. Numerous efforts have been made to reduce the temperature of hydrogen evolution (process called "activation"), but usually they all boil down to mechanochemical processing of studied hydride in the presence of a catalyst. These studies present only assertion of a catalytic effect but do not explain physical mechanisms in the background.

Both aluminium and magnesium hydrides are materials with ionic-covalent type of bonding; this determines the certain similarity of their desorption kinetics: significant incubation time and acceleration of hydrogen evolution after formation of the metallic nuclei. In the article these effects will be interpreted in the light of electronic structure data. Similar models will be discussed, which account for desorption and interphase reaction. Models satisfactorily approximate experimental data. Kinetic parameters are evaluated.

2. Experimental procedure

We used magnesium hydride obtained by direct synthesis from mechanically grinded magnesium and high purity hydrogen (99.999%) at a temperature of 670–740 K and pressures up to 30 MPa. The aged aluminium hydride (alane) was synthesized by chemical methods. Kinetics of dehydrogenation was studied using isothermal barometry and TDS methods. Hydrogen was released from the small-size autoclave into the temperature-controlled calibrated volume. Pressure range during experiments was 4–20 kPa. Reacted fraction (RF) was derived from the pressure measurements. The experimental procedure is described in detail in [6].

In the case of long-term desorption experiments with alane at low temperatures the fraction of reacted material was brought to 60–80% and then the sample was heated to a higher temperature (470–520 K) to assess the total amount of hydrogen and norm the results.

In part-by-part decomposition the sample was heated in several stages. At the first stage (let us call it "thermal activation"), the sample was rapidly cooled after it released 10–20% of its hydrogen. This led to the formation of metallic phase areas on the particle's surface (see below). During the subsequent cycles of heating and cooling the sample was brought to the pure metallic state.

3. Results and discussion

In Fig. 1 some experimental data and calculations for magnesium hydride are presented:

a. TDS of MgH_2 with heating rates of 0.2, 0.1, 0.05, 0.025, 0.01 K/s.
b. TDS of MgH_x, $x \sim 0.50$ (partially hydrogenated). Heating rates: 0.4, 0.2, 0.1, 0.05, 0.025 K/s.
c. Part-by-part decomposition of the stoichiometric MgH_2 hydride at 0.1 K/s.

Data presented in Fig. 1a and b have been published elsewhere [6].

In Fig. 2 some experimental data and calculations for alane are presented: a. Isothermal desorption in the range of temperatures

---

* Corresponding author.
E-mail address: igor.gabis@gmail.com (I. Gabis).

0925-8388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.12.080

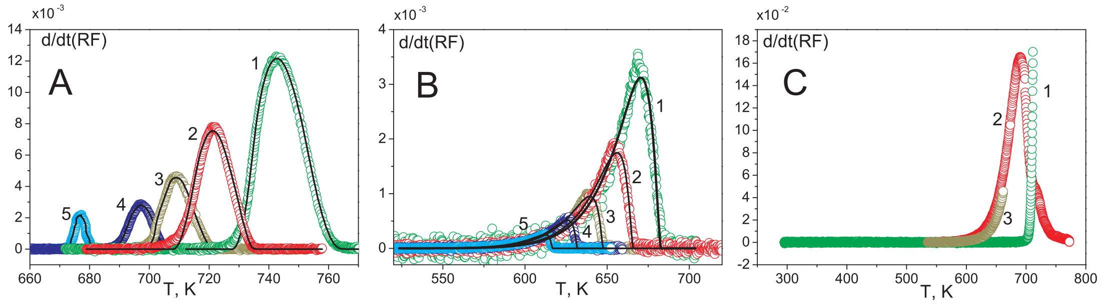

Fig. 1. Magnesium hydride decomposition data. Circles represent experiment, black lines represent calculations. (a) TDS of MgH_2 with heating rates of 1 – 0.2 K/s (green), 2 – 0.1 K/s (red), 3 – 0.05 K/s (olive), 4 – 0.025 K/s (dark blue), 5 – 0.01 K/s (light blue). (b) TDS of MgH_x, $x \sim 0.50$. Heating rates: 1 – 0.4 K/s (green), 2 – 0.2 K/s (red), 3 – 0.1 K/s (olive), 4 – 0.05 K/s (dark blue), 5 – 0.025 K/s (light blue). (c) Part-by-part decomposition of the stoichiometric MgH_2 hydride at 0.1 K/s. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

from 80 to 150 °C (353–423 K). b. TDS with heating rates of 0.01, 0.02, 0.05, 0.1, 0.2 K/s. c. TDS after thermal activation with rates of 0.02, 0.05, 0.1, 0.2 K/s.

On both figures d/dt(RF) is a derivative of a reacted fraction value, it corresponds to the rate of hydrogen evolution from the sample.

4. Features of desorption kinetics

In the isothermal experiments with alane (Fig. 2a) some delay was observed after the desired temperature of the sample was established and before hydrogen desorption started. The higher the temperature, the shorter this “incubation” delay. Results for MgH_2 were more impressive. At $T = 620$ K the incubation time exceeded 10^5 s.

Part-by-part hydrogen desorption from MgH_2 is shown in Fig. 1c. Here complete decomposition of the initially stoichiometric sample was reached in 3 steps of approximately equal duration. During the experiment each heating step was interrupted by cooling the sample to 523 K followed by its subsequent linear heating with the same heating rate. It can be seen that the first portion of hydrogen desorbs according to a typical scenario for MgH_2, i.e. a sharp desorption growth at ~700 K (compare with Fig. 1a, curve 2). Desorption of the second portion of hydrogen has similar features to H evolution from the partially hydrogenated samples – see Fig. 1b, curve 3. Clearly, this similarity originates from the alteration of the sample after desorption of the first portion of hydrogen, when the metal nuclei have been formed at the surface of the most particles.

Thermal activation, i.e. such heating of stoichiometric hydride followed by cooling creates small zones of the metallic phase in the particles of hydride. Aluminium and magnesium hydrides are materials with an ionic-covalent type of bonding. For this reason, desorption of hydrogen from their surface is very slow. Desorption of the first portions of hydrogen leads to the formation of metal nuclei on the hydride surface, which serve as a channel for facilitated desorption. This channel expands as hydrogen continues to leave a particle. As a result the temperature at which desorption begins during the successive heating decreases by 20–25 K (see Fig. 2c) in case of alane and by 100–120 K in case of MgH_2 (see Fig. 1c). In our opinion the ball-milling also leads to the formation of metallic nuclei due to a minor desorption of hydrogen.

5. Incubation

High rates of desorption and adsorption of hydrogen by metals are determined by the interaction of hydrogen and electronic subsystem of a metal. Significant concentration of free electrons in metals leads to their high catalytic activity in the processes of hydrogen surface dissociation and recombination. In contrast, the low concentration of free charge carriers (electrons and holes) in semiconductors and insulators determines their poor catalytic properties. We suppose that increase of free charge carriers concentration in studied hydrides at elevated temperatures leads to desorption of first portions of hydrogen by the end of incubation.

Aluminium and magnesium hydrides are wide-band semiconductors (band gap is 3.2 eV for AlH_3 [7] and 5.0–5.6 eV for MgH_2 [8,9]). At elevated temperatures the carriers' density is determined by two competing processes: the transfer of electrons from the valence band to the conduction band, and their return from the conduction band to the non-excited state in the valence band. The direct process requires overcoming the activation barrier equal to the width of the band gap. The rate of the reverse process usually does not depend on temperature. This leads to a gradual increase of electron density in the conduction band and thus an increase of catalytic activity of the material.

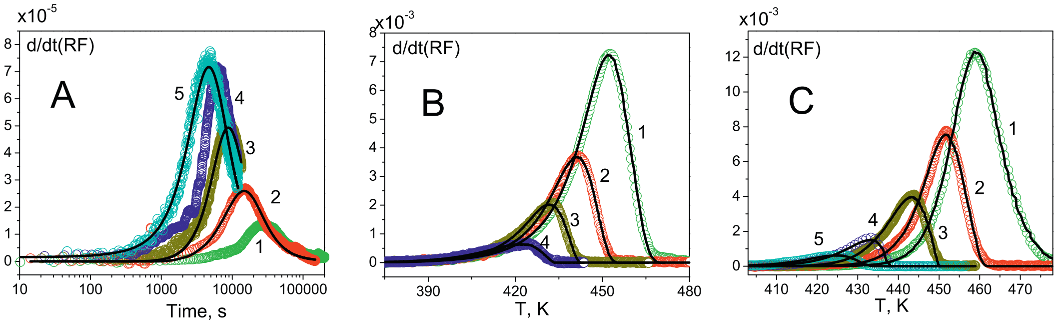

Fig. 2. Alane decomposition data. Circles represent experiment, black lines represent calculations. (a) Isothermal desorption at temperatures of 1 – 373 K (green), 2 – 383 K (red), 3 – 387 K (olive), 4 – 393 K (dark blue), 5 – 397 K (light blue). (b) TDS after thermal activation with rates of 1 – 0.2 K/s (green), 2 – 0.1 K/s (red), 3 – 0.05 K/s (olive), 4 – 0.02 K/s (dark blue). (c) TDS with heating rates of 1 – 0.2 K/s (green), 2 – 0.1 K/s (red), 3 – 0.05 K/s (olive), 4 – 0.02 K/s (dark blue), 5 – 0.01 K/s (light blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

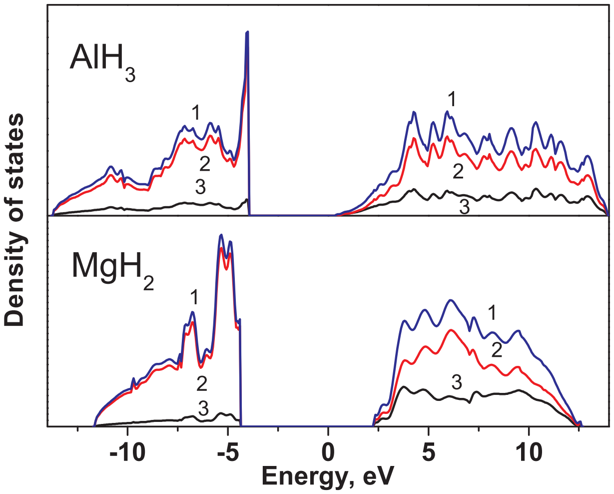

Fig. 3. Electron density of states (blue (1) – total, red (2) – hydrogen, black (3) – host metal). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

Our calculations (performed using the software package “Crystals” [10]) show that electrons are excited mainly from hydrogen states (but not metallic) in the valence band (see Fig. 3). It means that initially negative hydrogen ions incapable of surface recombination become neutral atoms. So during the incubation at elevated temperatures two processes increase the probability of H desorption:

1) increase of the concentration of free electrons in the conduction band,
2) change of hydrogen state from a negative ion to a neutral atom.

6. Diffusion

The diffusion of hydrogen in metallic aluminium is fast enough and doesn’t affect the overall rate of hydride decomposition. Evaluation of the diffusion coefficient in the temperature range of interest (370–420 K) gives the approximate value of $D = (2–10) \times 10^{-7}\,\mathrm{cm^2/s}$ [11], which means that diffusion time in the particle of average size $(1.0–1.5) \times 10^{-3}$ cm amounts to tens of seconds and cannot have any significant effect on the process. Moreover after hydrogen evolution a porous structure is formed (see Fig. 4b), and diffusion paths are even shorter.The same is true for magnesium hydride with $D = 3.8 \times 10^{-2} \exp(-4810/T)\,\mathrm{cm^2/s}$ [12] and size of particles 40–50 μm (see Fig. 4a, previously published elsewhere [6]). At elevated temperatures the time of diffusion is very low for it to limit the decomposition of hydride.

7. Modeling and fitting

Microscopic study showed that number of metallic nuclei formed during the initial stages of magnesium hydride decomposition is rather small, whereas in the alane there can be much more of them as is shown in Fig. 4. Moreover, the magnesium powder particles had a significant size distribution, while this distribution for the alane powder is rather narrow. These facts led to differences in mathematical processing of experimental data obtained for these materials. The results of mathematical approximation of experimental data were identification of the limiting process and evaluation of its kinetic parameters. For both hydrides we considered three cases of limiting stage: surface recombination, reaction on metal-hydride interphase, competition of both these processes.

In the case of magnesium hydride the morphology of a single particle decomposition is modeled as appearance and growth of a single isotropic nucleus from the surface of the particle into it’s bulk. Particle’s size distribution was taken into account, its parameters were fitted together with the kinetic parameters. Kinetics of dehydrogenation of activated magnesium hydride and the phenomenological model are described in detail in [6]. Limiting process is stated to be the desorption from the surface of metallic nuclei with activation energy $E = 185 \pm 10$ kJ/mole and pre-exponential factor $k_0 = (1.1–1.6) \times 10^{-11}$ cm/s. The solid lines in Fig. 1a–c show high quality approximation of experimental data.

In the case of the alane we applied the method of “morphological trajectories” [13]. It allows simulation of the continuous process of nucleation and subsequent growth of nuclei into the bulk. The model underlying the method of morphological trajectories considers three possible simultaneous reactions that may limit decomposition: nucleation, desorption, and reaction at the interphase, i.e. hydride decomposition. Detailed description of this model can be found in [13]. Rates of desorption from the metal aluminium and hydride decomposition are considered to depend on temperature according to the Arrhenius law, with nucleation having a certain probability. Thereby fewer nuclei are formed at heating with higher rates than with lower rates.

Application of the method shows that for alane limiting process is decomposition of hydride at the interphase boundary. Fig. 5 shows the Arrhenius plot of the metal-hydride interphase movement rate based on the set of isothermal desorption data (Fig. 2a). Activation energy of this process $E = 104$ kJ/mole and pre-exponential factor $k_0 = 1.4 \times 10^7$ cm/s. The solid lines in Fig. 2a show the results of approximation.

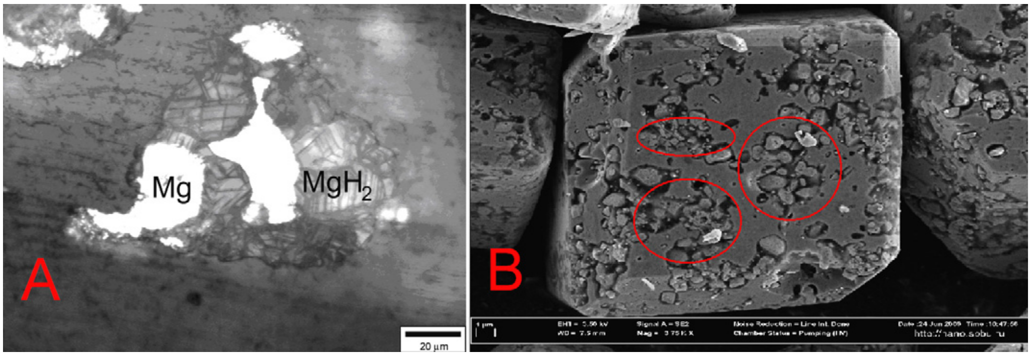

Fig. 4. Optical metallography of magnesium hydride and SEM of alane. (a) Magnesium hydride particle, decomposed by ∼40%. (b) Alane particle, decomposed by ∼20%. Red circles show clusters of metallic nuclei forming porous structure on the surface of the particle. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

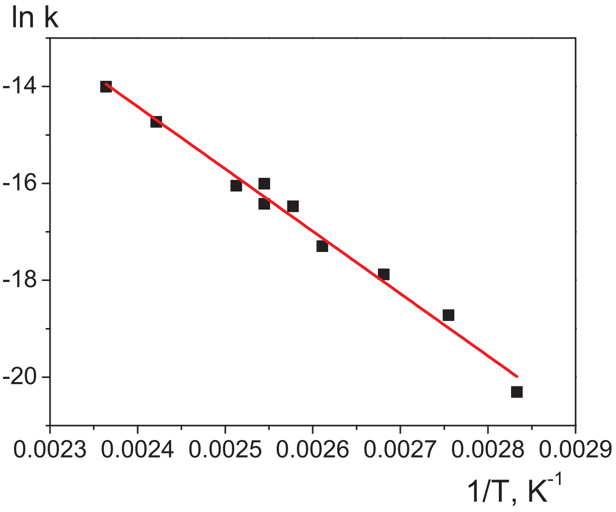

Fig. 5. Arrhenius plot of the metal-hydride interphase movement for alane.

Energy value mentioned above allows very high quality of approximation of the TDS curves obtained for inactivated and activated samples (see solid lines in Fig. 2b and c). Processing of this data gives nearly the same pre-exponential factors $k_0 = (1.1–1.8) \times 10^7$ cm/s.

After alane decomposition a porous structure of aluminium is formed (see Fig. 4b). Therefore only the nearest to the interphase regions of metal form areas available for desorption. Surfaces of these areas are comparable to the interphase surface. This consideration gives a possibility of an alternative interpretation of the experimental results: desorption from the surface of aluminium may play limiting role and control the metal-hydride boundary movement.

Experimental data from the present paper is quoted in the paper by J. Graetz et al. giving a broad overview of the status of the research on alane, which is published in this issue [14].

Conclusion

Similarities of electronic structures of alane and magnesium hydride allow the interpretation of their desorption kinetics properties from the common viewpoint.

Two factors can be responsible for increasing of desorption rate at elevated temperatures. Gradual increase of electron density in the conduction band leads to increase of materials' catalytic activity. Electrons are excited mainly from hydrogen states in valence band, changing the hydrogen from a negative ion to a neutral atom.

Metallic nuclei that appear on the surface of particles become channels for the facilitated hydrogen release. This channels expand as the desorption goes on.

Any method of creating areas of metallic phase on the surface of hydride, including thermal activation, increases the rate of hydride decomposition.

Kinetic parameters of limiting rates of magnesium and aluminium hydride decomposition are evaluated.

Acknowledgements

The work has been financially supported by the grant 09-03-00947 of the Russian Foundation for Basic Research.Interdisciplinary Resource Center for Nanotechnology, Saint-Petersburg State University.Department of Chemistry, Saint-Petersburg State University.

References

[1] B. Sakintuna, F. Lamari-Darkrim, M. Hirscher, Metal hydride materials for solid hydrogen storage, Int. J. Hydrogen Energy N. 32 (2007) 1121–1140.
[2] P.J. Herley, O. Cristofferson, R. Irwin, Thermal decomposition of alfa-aluminium hydride powder, J. Phys. Chem. 85 (1981) 1874–1881.
[3] I.M.K. Ismail, T. Hawkins, Kinetics of thermal decomposition of aluminium hydride: I-non-isothermal decomposition under vacuum and in inert atmosphere (argon), Thermochim. Acta 439 (2005) 32–43.
[4] G. Sandrock, J. Reilly, J. Graetz, W.-M. Zhou, J. Johnson, J. Wegrzyn, Accelerated thermal decomposition of AlH3 for hydrogen-fueled vehicles, Appl. Phys. A 80 (2005) 687–690.
[5] J. Graetz, J.J. Reilly, J.G. Kulleck, R.C. Bowman, Kinetics and thermodynamics of the aluminum hydride polymorphs, J. Alloys Compd. 446–447 (2007) 271–275.
[6] E. Evard, I. Gabis, V. Yartys, Kinetics of hydrogen evolution from α-MgH2: experimental studies, mechanism and modelling, Int. J. Hydrogen Energy 35 (2010) 9060–9069.
[7] M.J van Setten, V.A. Popa, G.A. de Wijs, G. Brocks, Electronic structure and optical properties of lightweight metal hydrides, Phys. Rev. B 75 (2007), 035204.
[8] C. Moyses Araujo, S. Lebegue, O. Eriksson, B. Arnaud, M. Alouani, R. Ahuja, Electronic and optical properties of α, γ, and β phases of MgH2: A first-principles GW investigation, J. Appl. Phys. 98 (2005), 096106.
[9] R. Yu, P.K. Lam, Electronic and structural properties of MgH$_2$, Phys. Rev. B 37 (1988) 8730.
[10] http://www.crystal.unito.it/.
[11] J. Topler, H. Buchner, H. Saufferer, J. Less-Comm. Met. 88 (1982) 397–404.
[12] E. Fromm, E. Gebhardt, Gase und Kohlenstoff in Metallen, Springer-Verlag, Berlin, 1976.
[13] E. Evard, A. Voyt, Hydride decomposition characterizaion by means of "morphological trajectories" method, application to AlH3, J. Alloys Compd., this issue.
[14] J. Graetz, J.J. Reilly, V.A. Yartys, J.P. Maehlen, B.M. Bulychev, V.E. Antonov, B.P. Tarasov, I.E. Gabis. Aluminum hydride as a hydrogen and energy storage material: Past, present and future, J. Alloys Compd., this issue.