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Cooperative effects at formation and decomposition of magnesium hydride in powders

I. Konstanchuk[a,*], K. Gerasimov[a], J.-L. Bobet[b]

[a] Institute of Solid State Chemistry and Mechanochemistry SB RAS, Kutateladze 18, Novosibirsk 630128, Russia
[b] Institut de Chimie de la Matière Condensée de Bordeaux ICMCB-CNRS, Université Bordeaux 1, 87 Av. Schweitzer, F-33608 Pessac, France

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ABSTRACT

The detailed kinetic analysis of formation and decomposition of powder magnesium hydride has shown that in contrast to conventional coarse-grained magnesium in which particles seem to react independently from each other, contacts between particles are important at hydriding of nanostructural magnesium because it facilitates the nucleation process hampered in nano-sized particles.

The cooperative effects have been revealed also at decomposition of powder magnesium hydride. Being limited by recombination and desorption of hydrogen, the reaction of decomposition of magnesium hydride starts on the particles containing metal impurities or being in contact with the metal surface of container. The nuclei of metallic magnesium formed in these particles initiate the nucleation in the neighboring particles being in contact with them. Nucleation propagates like a chain process. Separation of particles by dilution of the sample by inert additive leads to considerable decrease of the reaction rate.

1. Introduction

One of the main instruments for investigation and development of hydrogen storage materials is the kinetic analysis of hydriding and dehydriding reactions. Usually, in a typical investigation of the kinetics of "gas–solid" reactions the shape of the kinetic curves, together with the dependences of reaction rate on pressure, temperature and geometry (shape and size of solid particles) are used to determine the rate-limiting step and the mechanism of reaction [1]. Nevertheless, very often, the kinetic analysis is limited to the fitting of experimental kinetic curves with various formal equations of heterogeneous kinetics, which corresponded to the reactions with one or another rate-determining step. All empirical kinetic models, underlying these rate expressions, assume that all the particles of a solid reagent have the same shape with a narrow distribution of a grain sizes, react independently from each other and that the transformed fraction of each individual particle is approximately equal to the transformed fraction of whole sample (i.e. "single particle models").

Such assumption about the size and the shape of particles is hardly realized in a customary research of magnesium–hydrogen interaction. In this work, experimental confirmations of the assumption that particles of magnesium or magnesium hydride in a powder sample do not react independently from each other are demonstrated.

2. Experimental

Magnesium powder used in this work was 99.95% purity, with main impurities being iron, 0.017 wt.%, manganese 0.012 wt.%, copper 0.003 wt.%, aluminium 0.010 wt.% and zinc 0.006 wt.%. The hydrogen was obtained by decomposition of titanium–iron hydride.

Magnesium hydride obtained by hydriding procedure described in paper [2] consisted of approximately 95% MgH_2, the remaining part being magnesium.

Nanocrystalline composites were prepared by mechanochemical treatment of MgH_2 with catalytic (e.g. TiH_2) or inert (e.g. MgO) additives in a planetary ball mill under hydrogen atmosphere. The obtained composites were dehydrided and rehydrided several times for achievement of reproducible kinetic results.

Powders of MgO and MgF_2 were used for the dilution of the Mg or MgH_2 samples. The purity of these added compounds was 99.9%. These powders were previously heated at 873 K in a primary vacuum during 1 h to remove surface hydroxides and carbonates. It should be noted that identical results have been obtained at use MgO or MgF_2 in our experiments.

The crystalline structure, phase composition and crystallite size were determined by XRD analysis (Cu Kα radiation) with data processing by PowderCell 2.4 program.

The hydrogen absorption/desorption kinetics were evaluated using Sieverts type apparatus described elsewhere [2].

3. Results and discussion

3.1. Hydriding

The hydriding curves of both activated conventional coarse-grained magnesium and nanocrystalline magnesium cannot be

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* Corresponding author. Tel.: +7 383 339 93 47; fax: +7 383 332 28 47.
E-mail address: irina@solid.nsc.ru (I. Konstanchuk).

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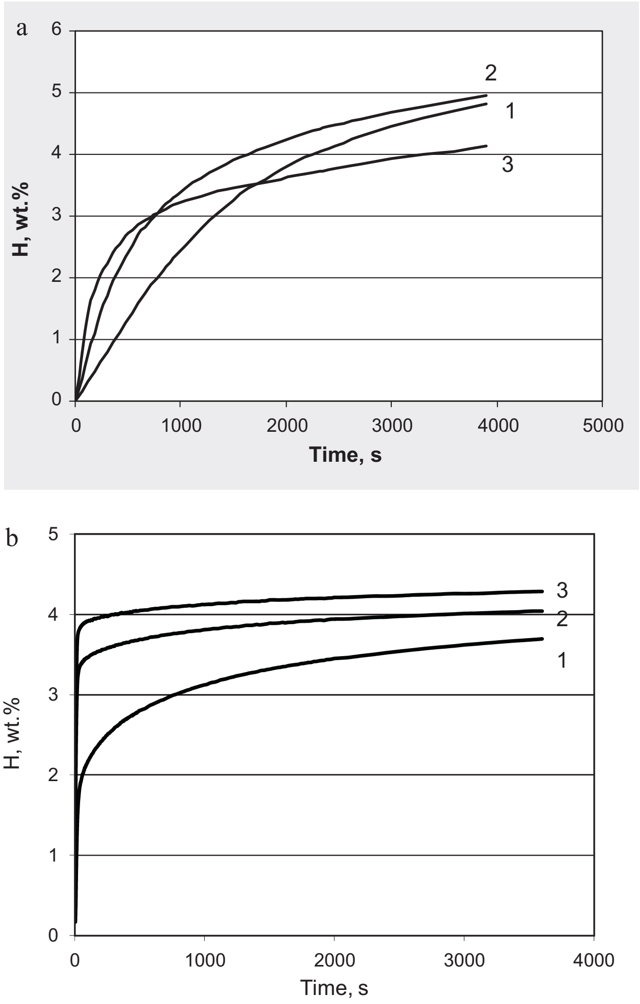

Fig. 1. The typical shape of kinetic curves at hydrogen absorption by coarse-grained (a) and nanocrystalline (b) magnesium (magnesium-based alloys and composites). (a) Mg–0.1 wt.%Ni coarse grained alloy activated by several hydriding-dehydriding cycles, T = 623K and P_{H_2}=0.63 MPa (1), 0.7 MPa (2), 1.65 MPa (3) and (b) Mg–10%TiH$_2$ nanocomposite at 373 K and $P_{H_2} = 0.2$ MPa (1), 1.0 MPa (2), 1.75 MPa (3).

fitted by any formal equations of heterogeneous kinetics. Moreover, the shape of hydriding curves of nanocrystalline magnesium differs from that of ordinary magnesium (Fig. 1). The characteristic feature of hydriding after activation of conventional magnesium (particle size more than 1 μm) is the regularity: the faster the initial rate of the reaction, the earlier the deceleration begins. As a rule such curves intersect with time (Fig. 1a). It is explained by the formation of tight layer of hydride on the magnesium surface which blocks further hydrogen absorption [3–5]. The increase of nucleation rate of magnesium hydride, for example, by means of enhancement of hydrogen pressure or addition of catalyst, leads to earlier nuclei overlapping and to earlier formation of tight layer of hydride.

Very fast initial rate of hydriding quickly decreases at certain degree of transformation in the case of magnesium-based nanocomposites (Fig. 1b). After a sharp bend, the kinetic curves become almost parallel and will intersect hardly each other. Contrary to expectation the full transformation of magnesium into hydride is not achieved in nanocrystalline composites especially at low temperatures.

Such behavior of kinetic curves hardly can be explained by the formation of surface hydride shell on the nano-particles of magnesium. More reliable explanation may be connected with the hampered nucleation of hydride phase in nano-sized particles of magnesium. Due to very low solubility of hydrogen in magnesium the number of hydrogen atoms dissolved in nano-sized particle of magnesium may be not enough for formation and growth of a critical hydride's nucleus. The part of the magnesium particles remains unreacted lowering hydrogen capacity.

In contrast to conventional magnesium the increase of hydrogen pressure leads to higher hydrogen capacity in the case of nanocrystalline magnesium. This confirms a supposition about the hampered hydride nucleation in nano-sized particles of magnesium. The hampered hydride nucleation explains also apparent "hysteresis" phenomenon observed for nanocrystalline magnesium-based systems [2].

The crystallite size in nanocomposites estimated from X-ray diffraction data was approximately 12–15 nm. Nevertheless, the individual powder particle reacting with hydrogen as whole apparently consists of several crystallites, and such particles also can be agglomerated in real samples. The possibility of diffusion of hydrogen from one particle to another cannot be ruled out even if particles boundaries impede this process.

To minimize the particle–particle interaction the magnesium samples were diluted by inert additives (MgO or MgF$_2$). It has been shown that the dilution of conventional magnesium by trituration in a mortar with the large quantity of inert additive (97 wt.%) has not changed the kinetics of hydrogen absorption in comparison with undiluted powders whereas the nanocomposites of Mg with same quantity of inert additive practically did not absorb hydrogen at the same experimental conditions. It means that the contact between nano-particles of magnesium facilitates nucleation of hydride phase. The cause of this phenomenon seems to be diffusion of hydrogen from a particle to another particle that forms quite a big quasi-particle behaving as a unit in hydriding process. The hydrogen absorbed on the interparticle interface in such quasi-particle can also promote the nucleation of hydride phase.

Unfortunately at present time we cannot estimate the quantity of hydrogen atoms necessary for formation of a stable nucleus of hydride in magnesium as well as the size of magnesium particle (or particles agglomerate) capable to dissolve such amount of hydrogen.

Our results are qualitative in character, but they all are consistent in the frame of supposition about the hampered nucleation of hydride phase in nano-sized magnesium.

3.2. *Dehydriding*

The rate-limiting step of decomposition of magnesium hydride is supposed to be the recombination and desorption of hydrogen on the magnesium surface [6]. Fig. 2 illustrates the dehydriding curves of the magnesium powder hydrided to different degrees of transformation – F. The dehydriding curves obtained for lower F represent parts of a curve 5 for the most hydrided sample. An acceleration and deceleration periods become more pronounced when the powder has been more hydrided. Finally, for the more hydrided samples (i.e. $F > 0.8$), the shape of desorption curves stops changing with increasing F. It means that unreacted magnesium core does not affect subsequent dehydriding in the most hydrided samples.

The Johnson–Mehl–Avrami (JMA) equation

$$1 - \alpha = \exp[-(k_1 t)^n],$$

with $n = 2$ [7] or $n = 3$ [8], has been reported to fit kinetic curves for decomposition of MgH$_2$ (α –transformed fraction at decomposition of MgH$_2$).

We found that a simple parabolic function

$$\alpha = k_2 t^2$$

even better describes the acceleration period [9].

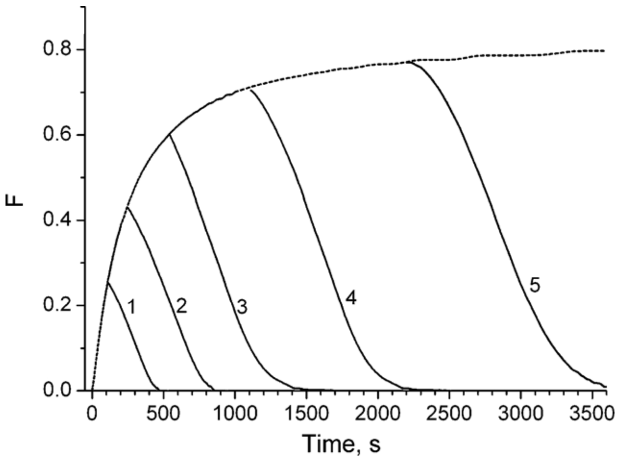

Fig. 2. Dehydriding curves of Mg powder hydrided to different F ($P_{H_2} = 0.02$ MPa, $T = 633$ K).

This can be interpreted as instantaneous nucleation followed by a two ($n = 2$) or three ($n = 3$) dimensional growth of the nuclei [7,8]. However, results of microscopic investigation of partially decomposed MgH_2 [3] showed that the assumption about instantaneous nucleation is far from being correct: the powder of MgH_2 decomposed up to $\alpha \approx 0.5$ consisted mainly of particles completely converted into magnesium and particles which not began to react yet.

Taking into account that hydrogen desorption rate is proportional to the area of a metal surface and from simple geometric constructions one can conclude that the constant velocity of the nuclei growth (that is usually attributed to an interface reaction as the rate-limiting step) is possible only in the case of three-dimensional growth of dense nuclei. So it is surprising that JMA equation with $n = 2$ as well as the parabolic function can fit kinetic curves of MgH_2 decomposition.

Moreover, contrary to expectation the apparent activation energy obtained for decomposition of the samples hydrided up to $F = 0.25$ and $F > 0.80$ turned out to be the same and equal to 164.0 ± 3.6 kJ/mol. It means that the contribution to activation energy from nucleation process, which must be considerably higher in the case of samples hydrided up to $F > 0.80$, did not appear.

The explanation of this fact can be made on the basis of the following assumption. The nucleation mainly takes place on contacts of unreacted MgH_2 particles with particles which have already formed magnesium nuclei. The hydrogen atoms recombine on magnesium surface of these contacts, i.e. the nucleation is a chain process.

According to this hypothesis, the kinetics of MgH_2 decomposition should drastically change if MgH_2 particles are diluted by an inert powder. Fig. 3 shows the kinetic curve for the third cycle of hydrogen desorption of MgH_2 (3 wt.%)–MgF_2 (97 wt.%) mixture, produced by trituration in a mortar.

One can see from Fig. 3 that the reaction rate decreases greatly and the shape of kinetic curve changes noticeably as a result of the dilution. The acceleration period of the decomposition curve can be well fitted with a function $\alpha = kt^4$. This can be accounted for a constant nucleation rate and a three-dimensional growth of compact Mg nuclei.

Thus the shape of kinetic curve of decomposition of MgH_2 powders depends in many respects on the contacts between the powder particles. Apparently, the reaction starts from the particles having a contact with metal impurities (Fe, Cu, Mn and others) commonly contained in magnesium and which can act as special location for a fast recombination of H atoms. After an initiation, a reaction front propagates over the entire powder bed through the contacts between the particles. Obviously, the contacts with sample holder can also act as the initiator of reaction front. The influence of container is usually neglected in the kinetic analysis on the basis of the fact that only negligible amount of the MgH_2 particles have contacts with container. This neglect would defensible if hydride particles decompose independently from each other. If contacts with sample container can act as the initiator of reaction front, the influence may be considerable as it is shown in Fig. 4 for powder containers made from stainless steel or corundum.

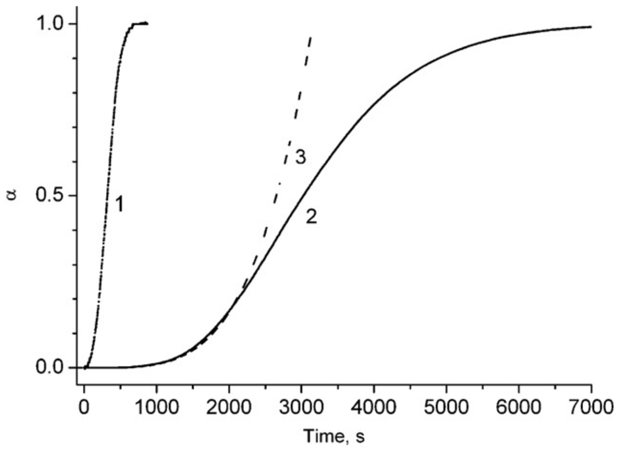

Fig. 3. Dehydriding curves at $T = 653$K and $P_{H_2} = 0.02$ MPa. (1) undiluted MgH_2 powder, (2) mixture MgH_2 (3 wt.%)–MgF_2 (97 wt.%) and (3) fitting of the acceleration period of curve 2 by the function $\alpha = kt^4$.

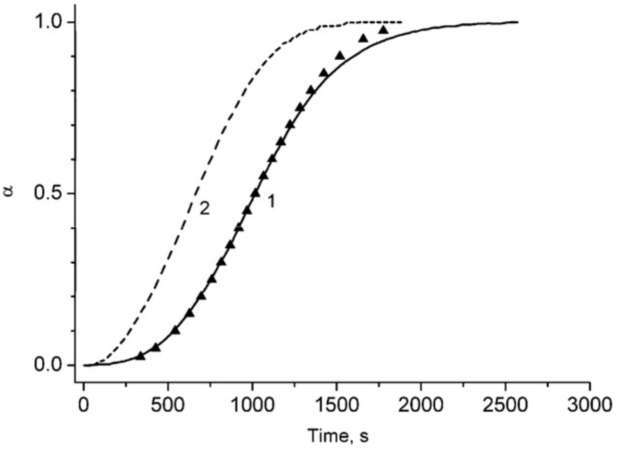

Fig. 4. Dehydriding curves of MgH_2 powder at $T = 633$K and $P_{H_2} = 0.02$ MPa: (1) in corundum container and (2) in steel container. Triangles show fitting by JMA equation with $n = 3$.

4. Conclusions

It has been shown that particles in the powder sample react not independently from each other during decomposition of magnesium hydride. The reaction starts on the particles containing metal impurities or being in contact with a metal surface of the container. The nuclei of metallic magnesium formed in these particles initiate the nucleation in the neighboring particles being in contact with them. Nucleation propagates like a chain process.

The material of the sample holder can affect the kinetics of reaction by initiating nucleation. It has to be taken into account at least when comparing results obtained at different experimental installations.

The cooperative effects do not appear at hydriding of conventional coarse-grained magnesium whereas the contacts between nano-sized magnesium particles facilitate nucleation process hampered at hydriding of nanostructural magnesium.

The separation of particles by dilution of the sample with inert additive leads to considerable decrease of the reaction rate at dehydriding.

Very diluted samples of nanostructural magnesium practically do not react with hydrogen.

All this has to be taken into consideration at developing hydrogen storage materials. Now the common opinion is that the good hydriding characteristics of magnesium-based materials may be achieved by means of reduction of particles down to nano-size. To prevent sintering of particles, various types of additives are proposed. But it became clear from our results that such additives seem to be effective only if they do not prevent hydrogen diffusion from one magnesium particle to another or if they serve as a catalyst of chemisorption/desorption by themselves.

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