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Magnesium-based materials for hydrogen storage: Recent advances and future perspectives

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Hydrogen storage is a real challenge for realizing "hydrogen economy" that will solve the critical issues of humanity such as energy depletion, air pollution, greenhouse emission and climate change. Recently, tremendous efforts have been devoted to this internationally focused area. Magnesium (Mg) is among the most promising candidates for this purpose and attracts numerous research interests. This paper is aiming at reviewing recent literatures on approaches and progress, the necessity of further research, and future direction to the research of Mg for hydrogen storage.

magnesium, hydrogen storage, hydrogenation, desorption

Rapid growth of energy demand and depletion of energy resources, and a successful strategy to tame greenhouse gas emissions highly require sustainable, renewable and clean energy. This leads to the strategy and initiation of the hydrogen economy. US Department of Energy (DOE) has proposed a US$1.7 billion first-five-year plan to start for hydrogen economy and its objectives will be achieved in several decades. Such an economy is that hydrogen is used for energy storage, distribution, and utilization. The key technological hurdles to the hydrogen economy include producing hydrogen economically, and storing and distributing hydrogen in a safe and effective manner. Following US hydrogen economy plan, many countries such as European countries (EU), China, Japan, including Australia, have invested big funds in sustainable energy research and development. For example, EU and Japan invested 275 million Euro and 30 billion Japanese Yuan in 2006[1]. Besides the governmental agencies, big companies such as GE, Toyota, Ford, BMW also devoted great efforts to developing hydrogen-driving cars because of the huge market of hydrogen which is expected to be US$35－55 billion (only in USA) in 2020[2]. In every stage of the hydrogen production to utilization in fuel cells, materials play crucial roles in achieving high conversion efficiency, safety, and robustness of the technologies involved. Among the most pressing issues, a major challenge to realize the hydrogen economy is the development of efficient and safe materials for practical hydrogen storage[3,4].

Hydrogen can be made available on board in several ways: compression, as a liquid, metal hydrides, chemical storage or gas-on-solid adsorption. Although each method possesses desirable characteristics, currently no approach satisfies all of the efficiency, size, weight, cost and safety requirements for transportation or utility use. For example, liquid hydrogen storage systems lose up to 1% a day by boiling and up to 30% during filling, as well as requiring good (bulky) insulation to keep the hydrogen at 20 K. Storage in a solid-state matrix, as a metal hydride for instance, has a safety advantage and is the current method for storage above room temperatures and below 2 to 4 MPa. The disadvantage of a metal hydride system is too stable that requires a high operational temperature for automotive applications. Physical adsorption of hydrogen onto an adsorbent is too unstable, generally requiring cryoadsorption, where the adsorbent is cooled to very low temperatures, to store large

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amounts of hydrogen. Although not as severe as liquid hydrogen, cryoadsorption suffers as an economic proposition because of the need to maintain such a low temperature[5,6].

Hydrogen storage in solid-state matrix, e.g. hydrogen storage materials such as nanostructural carbon[7−10], metal organic frameworks (MOFs)[11−14], metal hydrides[15−20], alanates[21−24], amides[25,26], and ammonia and ammonia borane[27−30], have not only their own advantages but also limitations to hinder their applications in some niche areas, in particular, for portable power facilities and in fuel-cell electric vehicles (FCEV)[1] that are a priority in the US Present's National Energy Policy. For example, highly porous solids such as zeolites, metal-organic frameworks (MOFs) and carbon nanostructures and related microporous solids, polymers have intrinsic microporosity, which is with the main favorable characteristics of fast kinetics and reversibility, but the major drawback is the low hydrogen capacity due to physisorption by weak van der Waals forces and thus this hydrogen adsorption often takes place only at a cryogenic temperature. By contrast, metal hydrides are generally too stable, which requires a high temperature to decompose. Adding a chemical element to simple metal hydrides, and forming so-called complex hydrides such as $LiBH_4$, $LiAlH_4$, $Mg(BH_4)_2$, is an effective method to destabilize the dehydrogenated state. Although this kind of materials is generally of high capacity but suffers from the critical drawbacks of irreversibility and sluggish kinetics.

Because of its vast extension and variety of hydrogen storage (solid) materials, it is impractical to review the whole field of hydrogen storage materials here. Magnesium (Mg) hydride (MgH_2) is widely regarded as a promising candidate for hydrogen storage materials under mild hydrogenation conditions due to its benefits of both high gravimetric and volumetric capacity, excellent reversibility, abundance in the earth and a low cost[31,32]. Accordingly, Mg and its based materials have been devoted great efforts and significant progress has been achieved in the last 3 decades. In this review article, we aim at reviewing recent advances in Mg-based materials for hydrogen storage, including the critical issues, recent approaches by use of catalyst, nanostructuring and alloying, and future perspectives on hydrogenation mechanism and hydrogen desorption of research in such materials.

1 Critical issues in hydrogen storage using Mg-based materials

An ideal hydrogen storage material for practical applications should obey five main commandments[33]: (i) high hydrogen storage gravimetric/volumetric capacity; (ii) ambient reaction temperature for charging/discharging hydrogen and fast kinetics; (iii) excellent reversibility; (iv) low cost and (v) low toxicity. With hydrogen, magnesium can form a hydride MgH_2 with a nominal capacity of 7.6 wt% of hydrogen in weight and ~110 kgH_2m^{-3} in volume; furthermore, a complex hydride Mg_2FeH_6 with the highest known volumetric hydrogen density of 150 kgH_2m^{-3}, which is more than the double of liquid hydrogen; and $Mg(BH_4)_2$ with a very high theoretical capacity about 14.8 wt% hydrogen. Magnesium and magnesium-based alloys are the most attractive materials that satisfy the main five commandments with high capacity, excellent reversibility, low cost and non-toxicity amongst all possible candidates. However, magnesium-hydrogen materials are limited for practical application so far due to their crucial limitations: (i) The temperatures for hydrogenation and dehydrogenation are too high. (ii) Both hydrogenation and dehydrogenation reactions are too slow.

In practice, both absorption and desorption of hydrogen require a temperature of at least 300℃ and over a time scale of a few hours, which is impractical for on-board applications[34].

There are several factors that significantly hinder the rate of hydrogenation. One is the oxidation of magnesium surface and/or formation of magnesium hydroxide[35]. Oxide layers on the metal surface are normally impermeable to hydrogen, preventing hydrogen from transporting into the materials. Another reason for the very low rate of hydrogenation of magnesium is the limited dissociation rate of hydrogen molecules into hydrogen atoms on the metal surface[32]. A clean surface of pure magnesium needs a very high energy for the dissociation. However, the dissociation barrier may be significantly reduced by the presence of a catalytic metal such as palladium[35,36]. In addition, the diffusion of the dissociated hydrogen atoms within metal hydrides is very difficult, thus reducing the particle/grain size of Mg, for instance, nanostructuring can significantly improve the hydrogenation of Mg. Another effective method is alloying Mg with other element such as Ni, which completely changes the thermodynamic property because of

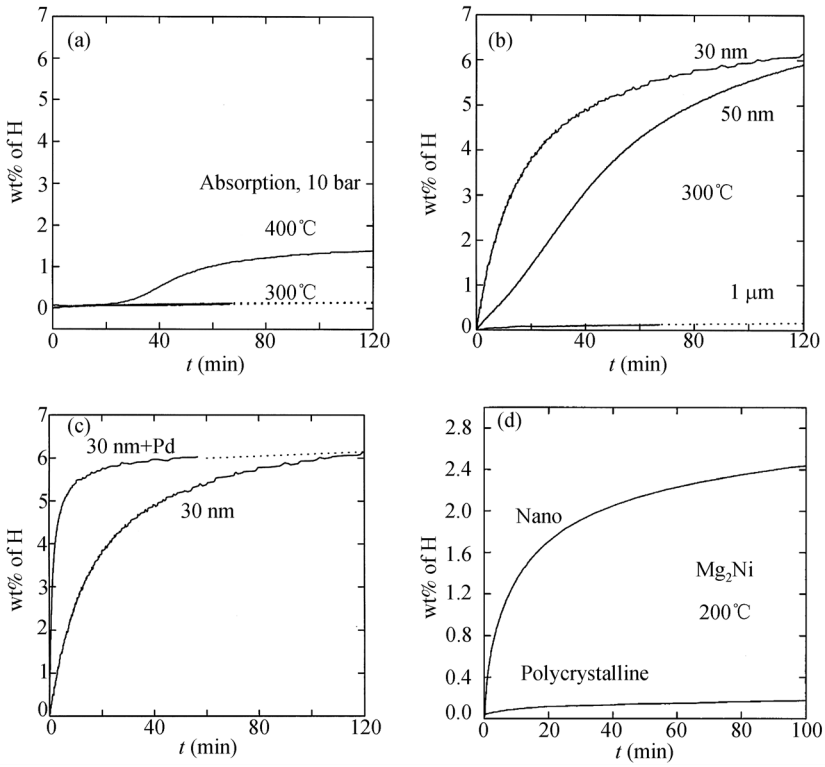

Figure 1 Hydrogenation of Mg. (a) Micro-Mg; (b) nano-Mg; (c) nano-Mg plus Pd; (d) Mg_2Ni[35].

the formation of a totally different compound, Mg_2Ni. However, this strategy suffers from the loss of theoretical capacity (3.6 wt% by Mg_2NiH_4 compared to 7.6 wt% by MgH_2)[37]. Figure 1 clearly shows the difficulty of hydrogenation of Mg at microscale (Figure 1(a): only 1.5% can be absorbed within 2 h at a temperature as high as 400℃) and the big improvement after nanostructuring (Figure 1(b)), use of catalyst (Figure 1(c)) and alloying (Figure 1(d)). In the next section, we will review the literatures of these approaches in improving hydrogen storage properties of Mg, mainly on the recent publications.

2 Approaches to enhance hydrogenation of Mg

2.1 Use of catalyst

The assistance of catalyst for hydrogenation of Mg has been extensively studied. The catalysts include transition metals[38−45], metal oxides[46−50], chemical compounds such as chlorides and inorganic compounds[51−55], intermetallic compounds that can absorb hydrogen[56−59], and carbon materials[60−64]. Why are catalysts necessary for Mg hydrogenation? Recently *ab initio* density functional theory (DFT) revealed that the catalyst completely changed the pathway of molecular hydrogen dissociation and significantly reduced the energy barrier for this process, which enables the hydrogen dissociation to occur at a very low temperature, such as room temperature[65–72]. As shown in Figure 2, hydrogen dissociation on pure Mg surface requires to overcome a high energy barrier of 1.05 eV, corresponding to over 300℃. However, the pathway of hydrogen dissociation has been

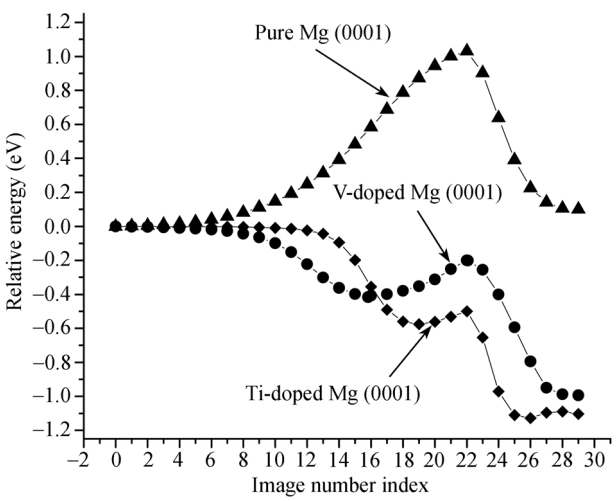

Figure 2 Energy profiles for hydrogen dissociation on Mg(0001) surface of pure Mg, Ti- and V-doped Mg[71].

optimized in the presence of metallic catalyst or metal oxide. The energy barrier has been remarkably decreased from 1.05 eV on pure Mg surface to 0.103 eV of Mg@Ti[66], 0.304 eV of Mg@V[71], 0.305 eV of Pd@Mg[70], and Mg@V_2O_5 is more effective for desorption due to the oxygen vacancies for hydrogen diffusion[72]. It is noted that C@Mg does not significantly influence the energy barrier of hydrogen dissociation[67], but carbon is effective additives to improve the hydrogen storage of Mg[73]. The reason is that carbon enhances the hydrogen diffusion and will be discussed later together with the behavior of metallic elements such as V, Ti, and Pd on hydrogen diffusion.

Carbon has attracted considerable interests due to the observation that the hydrogen storage performance of Mg could be improved by adding graphite (G)[60−64]. Due to their high specific surface area and unique adsorbing properties, nanostructured carbons synthesized by hard templating method such as CMK-3 have been shown to have a high catalytic dispersion and activity[74], and could be used for carrying nanoscale metal catalyst to be milled into MgH_2. Carbon nanotubes have been extensively studied for hydrogen storage[75,76]. Both mesoporous carbons and carbon nanotubes have a high surface area and consist of grapheme sheets. In our previous study, it was found that Mg-nanostructured carbon composites obtained by milling carbon with Mg had significantly increased the capacity of hydrogen storage[77,78]. As seen in Figure 3, carbon nanotube is the best additive that improves the hydrogen storage property at a low temperature of 150℃. Several possibilities explaining the prominent effect of carbon additives on the hydrogen storage of Mg are being considered: (i) the carbon is likely segregating at the grain boundaries during ball milling and thus increases the hydrogen diffusion along the boundaries; (ii) sub-layer carbon atoms may be formed by incorporating into Mg structures during ball milling, which will enhance the atomic hydrogen diffusion from surface to bulk Mg; and (iii) the dispersive feature of carbon may assist ball milling Mg to obtain finer Mg particles (grains) that shorten the diffusion path.

Recently, Yao et al.[71,79−81] reported that the coupling of transition metals such as FeTi, VTi, and MnZr has more significant effect on hydrogenation kinetics than the individual element alone. Experimental investigations demonstrated that these couples of elements remarkably increased the kinetics of Mg hydrogenation, especially at low temperatures which is very important for practical applications. The CNTs are more effective than other forms of carbons, which suggested that the residual CNTs with specific tubular structures may aggregate along the boundaries[71,79]. This specific structure will allow hydrogen to move inside the tubes of CNTs without any barriers, which is very helpful for hydrogen diffusion or transportation, in particular, at low temperatures. Consequently, Mg-CNTs system can achieve a higher hydrogenation capacity. More importantly, it is confirmed that the CNTs and the couples of transition metals have synergistic effect on hydrogen storage of Mg[71,79]. As seen in Figure 4, adding CNTs to Mg-FeTi system significantly increase the hydrogen capacity of the system. Interestingly, the effect of CNTs on the hydrogenation kinetics is completely different between high (300℃) and low (150℃) temperatures. As seen in Figure 5, at a high temperature, adding CNTs

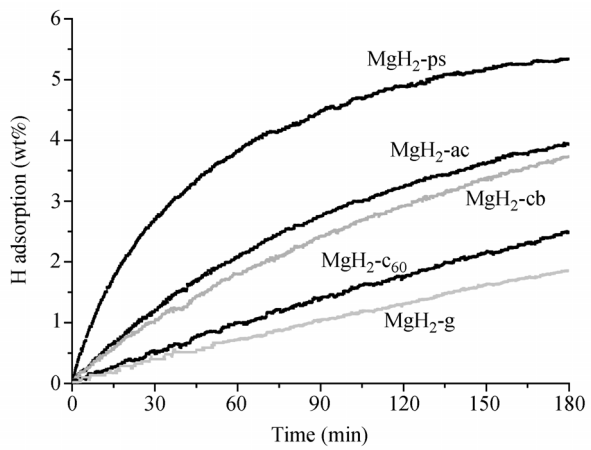

Figure 3 Hydrogenation kinetics of Mg with different carbon additives at 150℃.

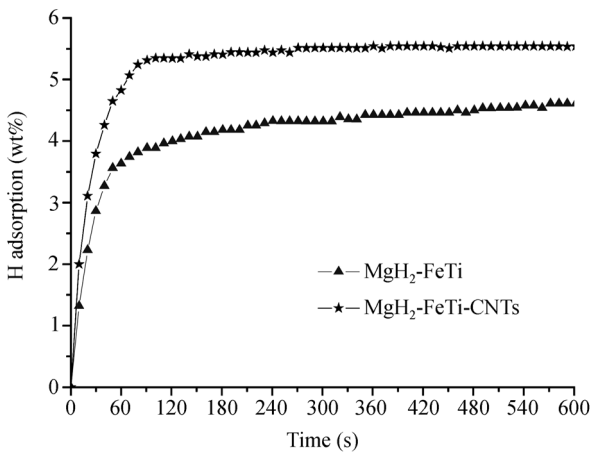

Figure 4 Synergistic effects of metal catalysts and CNTs on hydrogenation of Mg (measured at 300℃)[79].

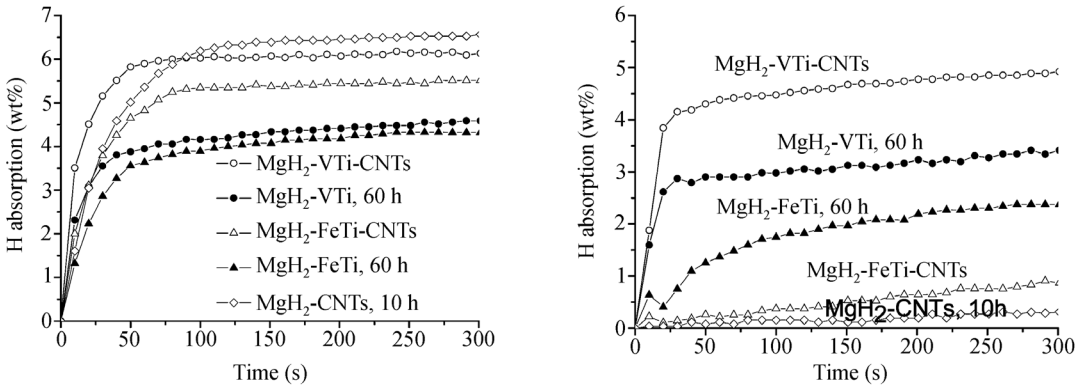

Figure 5 Hydrogenation kinetics of Mg in various Mg-catalyst systems at 300℃ and 150℃, respectively[71].

will further increase the hydrogenation kinetics. On the contrary, CNTs will hinder the hydrogenation at a low temperature. This can be explained that more catalytic sites for hydrogen dissociation on the Mg surface exist when C and Fe/Ti co-presented at a high temperature. However, at a low temperature, the C sites will be no longer effective for hydrogen dissociation because of the high energy barrier of C@Mg[67], but C occupies some sites on the Mg surface which reduces the number of FeTi@Mg sites and thus reduces the hydrogen dissociation rate of Mg-FeTi system. Therefore, the rate of hydrogen dissociation is an important factor to influence the hydrogenation kinetics of Mg. However, the situation is different in a presence of VTi. Adding CNTs will not decrease the hydrogenation kinetics even at a low temperature. It is explained that V is not only beneficial for hydrogen dissociation but also for hydrogen diffusion due to the easy migration of hydrogen atoms from V sites to Mg[71].

2.2 Nanostructuring

Once the molecular hydrogen dissociated into atoms on the Mg surface, hydrogen atoms will diffuse into Mg to form Mg hydrides (MgH_2). The diffusivity of hydrogen atoms within MgH_2 and the formation rate of MgH_2 on the Mg surface and/or along the grain boundaries (if any) are the key factors for hydrogenation capacity and kinetics. This is because the diffusion coefficient in MgH_2 is much smaller than that in Mg, such as, $\sim 10^{-18}$ compared to $\sim 10^{-8}$ m^2/s at 300℃[82,83]. Before the shell of MgH_2 formed around the Mg surface, the hydrogen atoms diffuse very fast in Mg, after which hydrogen diffusion becomes very slow and it is very difficult for hydrogen atoms to penetrate through the shell of MgH_2. It is reported that the hydrogenation rate of the remaining magnesium decreases with the increase of hydride layer thickness, and virtually becomes zero if the hydride layer exceeds a critical thickness[84]. Accordingly, for hydrogenation of Mg, the formation of MgH_2 is the controlling step before the shell is completely formed while the diffusion of hydrogen in MgH_2 becomes the control factor after the shell formation. The formation of MgH_2 is very complicated, associated with the nucleation and growth of MgH_2 nuclei and also the structure of MgH_2 and Mg (for example, defects such as boundaries inside Mg). The study on MgH_2 shell formation has not been reported so far and it is worthy of a future investigation.

Yao et al.[85] recently developed a mathematical model of hydrogen diffusion for MgH_2/Mg shell-core structure with assumption of rapid MgH_2 shell formation. Figure 5 shows that the diffusion coefficient of hydrogen within MgH_2 is in a range of $10^{-18} \rightarrow 10^{24}$ m^2/s at 300—100℃ and the activation energy for hydrogen diffusion in Mg hydrides can be easily calculated to be 107.9 kJ/mol. This value agrees well with data in a recent review by Sholl[82]. Using the data derived from this model, the effect of grain size on hydrogenation rate can be calculated as shown in Figure 6. At 150℃, the hydrogenation rate can achieve 1.96 wt% per minute if the particle (grain) size is of 3 nm. When the particle (grain) size increases, the hydrogenation rate remarkably decreases. It is required in practice that the rechargeable time should be in the scale of a few minutes. Accordingly, the relationship between the fraction of MgH_2 and the particle (grain) size by hydrided in 10 min at two different temperatures of 300 and 100℃ were plotted in Figure 7 (with assistant of hydrogen diffusion of grain boundaries and CNTs). It can be seen that at 300℃ only the particle (grain) size less than 65 nm can achieve the

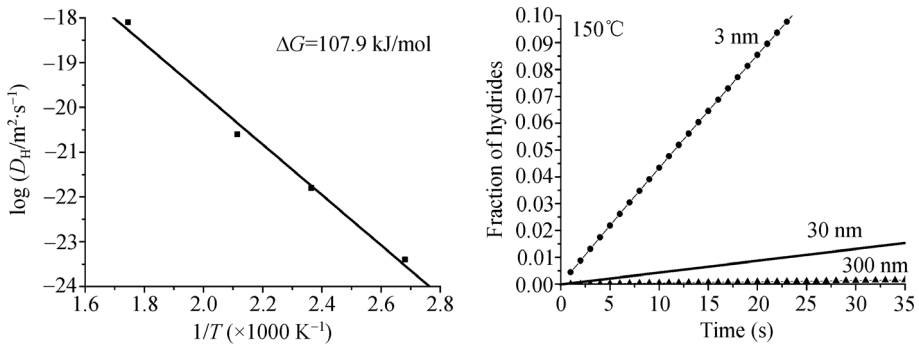

Figure 6 Temperature-dependent hydrogen diffusion coefficient in magnesium hydrides and the grain size effect on hydrogenation kinetics of Mg accordingly[85].

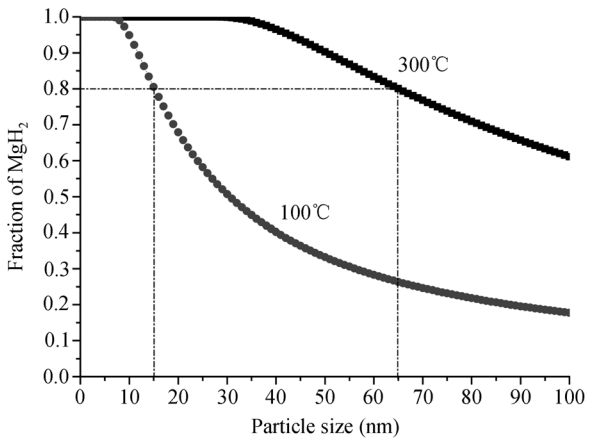

Figure 7 The relationship between the fraction of magnesium hydrides and the particle (grain) size in 10 min at 300 and 100℃, respectively.

DOE target on capacity of 6 wt%, while at 100℃ this value becomes less than 15 nm. It should be pointed out that the above calculated values should be less than the real critical thickness as the assumption of rapid formation of MgH_2 shell. The difference should become bigger for the larger particles (grains) due to the difficulty of forming integrate MgH_2 shell, allowing more time for hydrogen diffusion in Mg instead of in MgH_2. Although the critical thickness of MgH_2 shell could be larger, the fraction of MgH_2 will be decreased rapidly with the increase of the dimension of the particles (grains) due to the increasingly unhydriding inner part of the particles. It is concluded that it is impractical for the bulk Mg to be an efficient hydrogen storage material, which means that nanostructuring is necessary.

Nanostructured materials offer a host of promising routes for storing hydrogen in high capacity in compounds that have fast kinetics as shown in Figure 1[35]. The intrinsically large surface areas of nanophase catalyst can assist the dissociation of gaseous hydrogen, and the small volume of individual nanoparticles produces short diffusion paths to the materials' interiors. Nanostructured magnesium particles in conjunction with effective catalysts can overcome the high energy barrier of hydrogenation encountered in bulk phase and provide an extraordinarily high specific surface area, very short diffusion distance and grain boundaries that facilitate hydrogen absorption and transport. Through nanostructuring with favorable catalysts, it may be possible for hydrogenation to occur at a low temperature with rapid kinetics. In the last decade, a breakthrough in hydride technology was brought about by the preparation of nanocrystalline hydrides with high-energy ball milling. This method provides a good opportunity to improve hydrogen absorption/desorption kinetics due to the breaking of surface oxide layers and the exposure of fresh magnesium surfaces to hydrogen, the grain size effects and creation of defects that act as nucleation sites for the hydride phase formation and large grain boundary density that facilitates hydrogen diffusion in the matrix. It is impractical to review the ball milling method in developing hydrogen materials in detail here. Interesting readers can refer to previous review articles[86−88].

Although significant improvement in hydrogen storage property of nanostructured Mg-based materials has recently been achieved by ball milling, the grain size of the nanocrystallites synthesized is mainly in the range of 20−50 nm and with some exhibiting large crystals of the order of several hundred nanometers, which has been shown a hurdle for hydrogenation at low temperatures[79,80]. It is desirable to synthesize Mg-based materials with ultra fine nano-particles (grains), for example less than 15 nm, that will exhibit ultra fast kinetics according to the theoretical prediction, e.g. to achieve storing 6 wt% hydrogen in 10 min at a low temperature

such as 100—150℃. One of the possible methods to obtain such ultra fine Mg-based nanomaterials is to combine alloying element with Mg and the ball milling.

2.3 Alloying

Alloying another element with Mg to form a compound with different thermodynamic properties is an effective way to enable the hydriding/dehydriding at a less mild condition. This method is widely accepted in developing hydrogen storage materials. The most famous compound in this category is Mg_2Ni, which is actually the first magnesium-based alloy for hydrogen storage that was developed at Bruce-Haven National Laboratory in 1968[89]. Since then, Mg_2Ni has gained numerous research efforts as hydrogen storage materials[37,90—93]. For example, Zaluski et al.[37] fabricated Mg_2Ni-Pd nanocomposites by ball-milling to study their hydrogenation behavior. The hydrogenation kinetics is much better than that in Mg at low temperatures. However, this method always companied the loss of theoretical hydrogenation capacity, which is impossible for these materials to achieve DOE targets for the hydrogen capacity, e.g. 6 wt% in 2010. This is a critical weakness for its application in FCEVs although Mg_2Ni can be applied to other applications such as electrodes for rechargeable batteries[94].

Recently, amorphous and nanocrystalline Mg-Ni-Re alloys (Re=Y, Ce, La, Mm) produced by rapid solidification have attracted considerable interests for hydrogen storage materials due to the improvement of hydrogenation characteristics[95—98]. The rapid solidification technique can produce amorphous Mg-based alloys with the desirable composition for hydrogen storage. Through nanocrystallization, the amorphous phase transforms into nanostructured alloy. The grain size of such nanostructured alloys can be well-controlled and uniform in a wide range of grain sizes depending on the annealing temperature, time and heating rate[99]. However, the current research reported that the maximum hydrogen capacity was less than 5 wt% of the amorphous or nanocrystalline Mg-Ni-Re alloys because of the large amount of Ni and Re and the relatively large grain size of 100—150 nm. Therefore, it is desirable to re-design the alloy composition and improve the fabrication method. More recently, Yao et al.[100] have developed ultra fine Mg-based nanocomposites by ball milling the amorphous Mg-10Ni-5Y with newly developed nanocarbon supported metallic catalyst, at an average grain size of ~4.7 nm and dispersed with Mg_2Ni nanoparticles at a size of ~2.7 nm. This system exhibits ultra fast hydrogenation kinetics and achieves a maximum hydrogen capacity of 6 wt%, which is worthy of further investigations to optimize the alloy compositions and fabrication technology.

3 Future perspectives

Continuing the research interest of Mg for hydrogen storage materials, several important aspects, such as hydrogenation mechanism, hydrogen desorption, hybrid materials of Mg and other hydrogen storage materials[101], destabilization of Mg[102], etc., should be addressed for future investigations. In this review, we will focus on the hydrogenation mechanism and hydrogen desorption of Mg-based materials. This is because the hydrogenation process of Mg is very complicated and the hydrogenation mechanism has not been fully understood, and hydrogen desorption becomes the "bottle neck" of application of Mg to practical hydrogen storage when the recent research enables the fast hydrogenation at a low temperature[71].

3.1 Hydrogen mechanism

Basically, the hydrogenation of Mg can be divided into three key steps: hydrogen dissociation, hydrogen diffusion and MgH_2 formation. Each step can influence other steps to make the processing more complex. The first step of hydrogen dissociation is relatively simple as this sub-process only involves the interaction of gaseous hydrogen and metallic atoms on the Mg surface. It will reduce the energy barrier remarkably and the hydrogen dissociation that the atoms of catalysts are incorporated into the Mg surface, and thus can occur at a low temperature, which enables hydrogen absorption thermodynamically possible at this temperature. The second step of hydrogen diffusion is much more complex as besides the temperature many other factors such as structure (defects such as vacancies and grain boundaries), materials (Mg or MgH_2), hydrogen dissociation rate and the hydrogen pressure (initial concentration of hydrogen atoms on the Mg surface), grain boundary modifications (segregating carbons) and catalytic elemental atoms (for example, V are reported to be also effective to enhance hydrogen diffusion because the bonding characteristics with H, and Mg-VTi-CNTs system demonstrated ultra

fast hydrogenation kinetics[71]) are involved. The third step of MgH_2 formation is also complex because of the interactions between the formation of MgH_2 and the hydrogen diffusion and the morphology and structure of MgH_2 around the Mg surface and along the grain boundaries. Hydrogenation mechanism remains many unclear issues on which the research is highly desirable to be performed by both theoretical modelling such as DFT calculations, quantum chemistry/quantum mechanics calculation and experimental investigations.

3.2 Hydrogen desorption

Followed by the significant improvement of hydrogen absorption kinetics, hydrogen desorption becomes more critical for application because the recent approaches by use of catalyst and nanostructuring can only reduce the desorption temperature to around 300℃ at hydrogen atmospheric environment although some publications reported that the hydrogen desorption could occur at ~220℃ under hydrogen free surroundings[60,103]. The temperature of around 300℃ is too high to be applied for FCEVs and future efforts on lowering the desorption temperature are highly required.

Generally, it is simple to deduce that the standard enthalpy of desorption (ΔH_{des}) of a binary hydride may serve as an approximate quantitative predictor of the desorption temperature (T_{des}). Considering the decomposition reaction of a metal (M) hydride as

$$\mathrm{MH}_n \rightarrow \mathrm{M} + (n/2)\mathrm{H}_2(\mathrm{g})$$

with the associated thermodynamic parameters of

$$\Delta G_{\mathrm{des}} = \Delta H_{\mathrm{des}} - T_{\mathrm{des}}\Delta S_{\mathrm{des}},$$

where ΔG_{des} and ΔS_{des} are the standard Gibbs energy and the entropy change for the decomposition reaction, respectively. ΔS_{des} approximately equals to the entropy of molecular hydrogen, 90—130 J/(mol·K)[104−106]. When the decomposition reaction occurs, ΔG_{des}=0. Therefore, the T_{des} can be simply calculated as $T_{\mathrm{des}} = (\Delta H_{\mathrm{des}} / n)(2/\Delta S_{\mathrm{des}})$. The detailed description of this thermodynamic theory can be found in a comprehensive review of Grochala and Edwards[33], which matches well with the experimental measurements. For MgH_2, ΔH_{des} has been measured experimentally as 76.15 kJ/mol, and T_{des} can then be calculated as 312−570℃, which reasonably agrees with the experimental results of above 350℃[33,34]. According to the theory, it can be easily calculated that the desorption temperature of MgH_2 at 150℃ requires ΔH_{des} in the range of 38−55 kJ/mol.

Accordingly, the desorption temperature of MgH_2 can be tuned through modification of thermodynamic property, ΔH_{des}. An effective way to modify ΔH_{des} is alloying as discussed before, for example, Mg alloying with Ni to form Mg_2Ni and ΔH_{des} of hydrogen releasing from Mg_2NiH_4 is ~40 kJ/mol but at the cost of a partial reduction of gravimetric capacity. Reducing particle/grain size has been reported to modify the thermodynamics in other systems due to the surface energy and nanograin boundary[107] and this method may be applied to Mg. It is also theoretically suggested that the confinement by CNTs on Mg/MgH_2 system can reduce hydrogen desorption temperature[108–111]. However, the understanding of hydrogen desorption mechanism is very limited and the research extension is highly desirable.

4 Conclusion and future directions

Mg is a promising candidate for hydrogen storage materials but limits its applications by high operational temperature and slow kinetics. Tremendous efforts have been devoted to overcome these two obstacles. By use of catalyst, nanostrucutring and/or alloying, remarkable improvement has been obtained in increasing hydrogenation kinetics, in particular, at a low temperature, which demonstrates that the limitation of slow kinetics of hydrogenation can be removed but further investigation is required. However, hydrogen desorption in Mg-based system still remains a critical high temperature, which is now the only barrier for practical application. Reducing the desorption temperature by modifying the thermodynamics of Mg and its based materials should be focused in future researches. Reducing the particle/grain size in nanoscale, increasing the density of defects, partial alloying with other element, confinement by porous materials, surface modification and selection of powerful catalyst might be the effective ways to realize this purpose of reducing hydrogen desorption temperature of Mg.

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