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REVIEW

An overview of progress in Mg-based hydrogen storage films*

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Mg-based hydrogen storage materials are considered to be one of the most promising solid-state hydrogen storage materials due to their large hydrogen storage capacity and low cost. However, slow hydrogen absorption/desorption rate and excessive hydrogen absorption/desorption temperature limit the application of Mg-based hydrogen storage materials. The present paper reviews the advances in the research of Mg-based hydrogen storage film in recent years, including the advantage of the film, the function theory of fabricating method and its functional theory, and the influencing factors in the technological process. The research status worldwide is introduced in detail. By comparing pure Mg, Pd-caped Mg, non-palladium capped Mg, and Mg alloy hydrogen storage films, an ideal tendency for producing Mg-based film is pointed out, for example, looking for a cheap metal element to replace the high-priced Pd, compositing Mg film with other hydrogen storage alloy of catalytic elements, and so on.

Keywords: Mg-based hydrogen storage film, Pd-caped Mg film, Mg alloy film, interlayer, intermetallic, co-operative effect

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1. Introduction

As a very important functional material, hydrogen storage materials play an irreplaceable role in the field of secondary energy, especially in the research of fuel cells and rechargeable batteries. The study of hydrogen storage materials is directly related to the application of electric vehicles, and also has an important impact on submarines, spacecraft, and other fields. Mg-based hydrogen storage materials are considered to be one of the most promising solid-state hydrogen storage materials due to their large hydrogen storage capacity and low cost. However, the formation enthalpies of hydrides of Mg and its alloys are too high that the hydrogen absorption/desorption starts only at temperature up to 623–673 K and it takes up to a few hours for the complete hydrogenation. Therefore, reducing the hydrogen absorption/desorption temperature and improving the kinetic performance of Mg without significantly changing the high hydrogen storage capacity of Mg has become the focus of current research. In order to overcome these shortcomings of Mg-based hydrogen storage materials, various modification methods have been studied, for example, additive modification, element substitution, nanostructuring, etc.[1–25] During this process, it was observed that grain refining to the nanoscale is one of the effective methods for improving the hydrogen absorption/desorption kinetics of Mg-based materials in spite of a decrease in reversible storage capacity.[26,27] Effects induced by decreasing grain size include: (I) increased specific surface area leads to increased surface energy and promotes chemisorption of hydrogen;[28,29] (II) increased grain boundaries provide channels for the diffusion of hydrogen atoms between grains; (III) due to the fact that nucleation and growth of the hydride phase (β phase) generally first occur on the surface of the grain and the diffusion rate of hydrogen atoms in the hydride phase is much lower than that in the solid phase (α phase), the hydrogenation reaction diminishes completely when the hydride layer exceeds 30–50 μm, which results in incomplete hydrogenation. Reducing grain size down to nanoscale allows shortening the diffusion distance of hydrogen atoms in the hydride phase, thereby increasing the formation rate of hydride.[4,6,30] Ball milling is a widely used method for refining grains to the nanoscale, improving absorption/desorption kinetics, and allowing easy mixing with catalysts.[16,31–34] However, there are some disadvantages of using ball milling for hydrogen storage applications, including long milling times, the presence of oxides, contamination from the milling environment, and powder size limitations ($>$ 80 nm).[35,36] In addition, the cycling stability of the particle hydrides decreases due to decrepitation and intergranular segregation associated with the repeated swelling and shrinkage of the hydrides upon absorption and desorption of hydrogen.[37] Such mechanical issues can be avoided by confinement of the storage material in porous matrices or by shaping it as thin films. Compared with ball milling, the main advantage of thin film nanostructuring is that it is easier to control the crystal structure, such as amorphous structure, nanocrystalline, and columnar structure in order to study influence of microstructure on properties of magnesium

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hydride.[38–40] Compared with bulk hydrogen storage materials, the hydrogen storage materials in the form of films have the following advantages: (i) fast rate of hydrogen absorption/desorption, (ii) high thermal conductivity, (iii) relatively easy surface-modification of the film, such as surface ion bombardment, electroless plating, etc., and (iv) surface covering protection which prevents oxidation of thin film and plays the catalytic role as well.[35] In this paper, we introduce preparation methods and structures of Mg-based hydrogen storage films and pay especial attention on introducing types of Mg-based hydrogen storage films and analyzing their respective advantages and disadvantages in terms of structure and hydrogen storage properties. By reviewing these data, we hope this paper can help more researchers better understanding Mg-based thin films, and shed light on further work.

2. Methods for preparing Mg-based alloy film

Physical vapor deposition (PVD), including vacuum vapors transport and sputtering deposition, is the most commonly used method for the preparation of Mg-based thin films. There are a series of sputtering methods, for instance, according to the presence or absence of an applied magnetic field, sputtering is divided into magnetron sputtering and non-magnetron sputtering; according to the type of current of power source, sputtering can be divided into direct current (DC) sputtering and radio frequency sputtering; according to the presence or absence of reactive gases during sputtering, sputtering is divided into reactive sputtering and non-reactive sputtering; according to the continuity of the current of power source, sputtering can be divided into continues sputtering and pulsed sputtering.[41–51] If the plasma is not generated by the bombardment of the particles, which are accelerated in the electric field, with the target, but by the interaction of pulsed laser with the target, then the deposition is called pulsed laser sputtering deposition or pulsed laser deposition (PLD).[52,53] For Mg-based thin films, hydrogenation can be achieved in two ways: air-exposed hydrogenation and plasma-based hydrogenation, which is realized in reactive sputtering. In addition, if between film deposition process and plasma-based hydrogenation film is air-exposed, then the deposition is called plasma-based *ex situ* hydrogenation. On the contrary, if the film deposition process is continuously followed by plasma-based hydrogenation or these two different processes simultaneous proceed, this kind of hydrogenation is known as plasma-based *in situ* hydrogenation.[54,55] When preparing a hydrogen storage thin film by vacuum vapor transport, special vaporization technology must be adopted because the vapor pressure of each metal component is different at a certain temperature. According to the number of evaporation sources, vacuum vapor transport can be divided into flash evaporation and continuous evaporation. In flash evaporation, the alloy to be evaporated is made into powder, and gradually shaken off to a high-temperature evaporation source in a small amount to ensure that the metallic components of the alloy are completely evaporated instantaneously and deposited on the substrate. The film produced by this method is substantially identical to the original material in terms of composition and usually has an amorphous structure. Continuous evaporation system is equipped with two independent evaporation sources, on which different metallic components of the alloy are evaporated simultaneously. An alloy film of an appropriate composition ratio can be produced on the substrate by controlling the temperature of each evaporation source. The disadvantage of the vacuum vapor transport is that the evaporation rate is difficult to control, the adhesion of the film to the substrate is not good, and a special evaporating dish is required for the material with a high melting point. The sputtering method combines the advantages of flash evaporation and continuous evaporation that when preparing the hydrogen storage alloy film, the target system may be an alloy target or independent targets made of each metal component. Comparing some mechanical properties of $LaNi_5$ films prepared by sputtering and flashing evaporation, Sakaguchi *et al.*[56] found that by using the sputtering method, the obtained film had a larger density and hardness and the adhesion of the film to the substrate was also stronger. In addition to different evaporation methods, different sputtering methods also have their own advantages, for example, equipment for direct current sputtering is simple and allows fast rate of metal sputtering, while radio frequency sputtering can be more widely used not only for conductive materials but also for nonconductive materials. The advantage of reactive sputtering is that during sputtering, mixed Ar–H_2 plasma is employed, which effectively avoids oxide formation.[40,57] However, it is noteworthy that although the sputtering method overcomes some of the shortcomings of the vacuum vapors transport method, there are still several disadvantages, for example, during the film formation process, the substrate contacts the plasma, and the film layer is continuously bombarded by gas atoms and charged particles, so that the substrate is prone to be heated, and the film layer often contains impurities of discharge gas.[58]

3. Research progress

3.1. Mg film

3.1.1. Pure Mg film

Bulk Mg has poor hydrogen absorption/desorption activity and usually requires temperature up to 620 K to release hydrogen. The Mg film is composed of nanocrystals and amorphous crystals, in which the diffusion rate of hydrogen is fast, thereby accelerating the hydrogen absorption/desorption rate. The microstructure and hydrogen storage properties of Mg

film are controlled by deposition parameters, such as gas pressure (the total pressure and hydrogen partial pressure of the Ar–H_2 gas mixture for reactive sputtering), the sputtering rate of Mg, the substrate temperature, and the deposition process model.

Typical features of films prepared by PVD are nanocrystals and columnar structures, which are associated with deposition rate of Mg film and the substrate temperature. In the early stage of deposition, the Mg particles reach the surface of substrate, the temperature of which is relatively low but the temperature of Mg particles is so high that the cooling rate is extremely fast, resulting in a weak mobility of Mg particles with a high nucleation rate. As a result, a large amount of dispersive tiny grains are dispersed on the surface of the substrate until the grains cover the entire substrate surface to form a continuous dense morphology. After that, the Mg particles reaching the substrate will be deposited on the tiny Mg grains with higher temperature, thereby the cooling rate is reduced and the diffusion time of the atoms is increased. Under this condition, the grains have an anisotropic growth tendency, which possibly leads to a deposition process with a certain preferred growth orientation, thereby forming a columnar structure.[38,59–61] Studies show that compared with continuous dense morphology, columnar structure is detrimental to hydrogen storage capacity.[62] Moreover, as the thickness of the Mg film increases, the porous columnar structure increases, which results in a raise of hydrogen desorption temperature.[63] Another point to note is that the preferred orientation of columnar structure also exerts an influence on hydrogen storage properties of Mg film. Leon *et al.*[64] reported that for Mg, which has columnar structure highly oriented along the [002] direction, the kinetics of hydrogen absorption/desorption are faster compared with that of Mg film with dispersive columnar structure in different directions. The type of substrate exerts little effect on the microstructure of the Mg film, but it was observed that new phases generated by the reaction of Mg and substrate drastically destabilized MgH_2.[38,62,65] In addition, the surface properties of substrate significantly influence the hydrogen absorption/desorption properties of pure Mg film. Lelis *et al.*[66] reported that plasma treated Si substrate seriously inhibited the formation of magnesium hydride phase. This is mainly attributed to that the plasma treatment leads to an increase of the substrate temperature, thereby increasing the size of columnar structure. This phenomenon is consistent with the influence of columnar structure on hydrogen storage capacity reported by the reference.[62]

In addition to the microstructure of pure Mg film, different preparation methods as well have various effects on the hydrogen storage properties of pure Mg film. Unlike traditional methods of preparing Mg-based hydrogen storage materials, in pure Mg film prepared by magnetron sputtering as a result of plasma based *in situ* hydrogenation, MgH_2 phase is formed near substrate-film region instead of on the surface of film.[54,67,68] Besides, compared with Mg film prepared by thermal evaporation, the Mg film prepared by magnetron sputtering is more easily oxidized in the air so that it is difficult to be hydrogenated using plasma-based hydrogenation approach after being exposed to the air.[54,60]

3.1.2. Pd-capped Mg thin film

Although due to the size effect, the hydrogen absorption/desorption properties of pure Mg film have been improved compared with bulk Mg, both the complete absorption and desorption of hydrogen require a temperature of at least 573 K and 673 K, respectively. Moreover, the high hydrogen storage capacity observed in the fist hydrogen absorption decreases in the subsequent cycles of hydrogen absorption/desorption.[60,69] Pd has a good hydrogen absorption/desorption activity ($T < 400$ K) but a low hydrogen storage capacity, which is only 0.6 mass%; on the contrary, the metal Mg has a high hydrogen storage capacity of up to 7.6 mass% but poor kinetics properties. In order to make up for respective shortcomings of Mg and Pd, a Pd-capped Mg thin film with better hydrogen storage capacity and hydrogen desorption activity was obtained. In Pd-capped Mg thin film, Pd can act not only as a protective layer to prevent oxidation of Mg in the air and interaction of Mg with the substrate, but also as a catalyst in enhancing the rate-limiting dissociation of hydrogen molecules at the sample surface, thereby effectively reducing the hydrogen absorption/desorption temperature, allowing possibility of hydrogen absorption below 373 K and hydrogen desorption below 473 K.[70,71]

Gautam *et al.*[72] prepared Pd-capped Mg thin films using DC magnetron sputtering and found that hydrogen absorption stars at 423 K and reached a maximum at 523 K. However, it is worth noting that unlike pure Mg film in Pd-capped Mg thin films, the MgH_2 phase forms epitaxially relative to Mg/Pd interface, which results in an anomalous phenomenon along with hydrogen absorption/desorption in Mg/Pd thin film, i.e., the reduction of hydrogen absorption rate with the increase of hydrogen pressure[73,74] due to the "blocking effect",[75] and suggests the hydrogen diffusion process, thereby the nucleation and growth of hydride phase is the rate determining step in Mg/Pd films in low temperature.[76] Reddy *et al.*[77,78] reported that Mg/Pd film can form Mg–Pd intermetallic compounds in high temperature resulting from reactive diffusion between Mg and Pd, which benefits the cyclic stability of film but has a negative impact on the kinetics. They attributed this kind of influence to the fact that intermetallic compounds occupy grain boundaries of Mg, which are channels for hydrogen diffusion. The Mg–Pd intermetallic compounds in Mg/Pd

films were also observed by other groups.[78–81] Unlike Reddy *et al.*, Ares *et al.*[57] used an interface mechanism to explain the influence of Mg–Pd intermetallic compounds on kinetics. They believed that it was the Mg_6Pd/MgH_2 interface having a higher activation energy than that of Mg/MgH_2 that limits the interface migration rate, thereby limiting the kinetics of Mg/Pd film.

Gharavi *et al.*[82] investigated the influence of the thickness of Mg film on hydrogen absorption/desorption properties of Mg/Pd film. They found that decreasing the thickness of the Mg film leaded to a lower hydrogen absorption/desorption temperature as well as a fuller hydrogenation/dehydrogenation. Under the condition that the thickness of the Mg film was reduced to 200 nm, a full hydrogenation/dehydrogenation of Mg/Pd film was achieved in low temperatures below 423 K.

Singh *et al.*[53] found columnar structures with different orientations in Mg/Pd film like that in pure Mg film, and they contributed this small variation in orientation of the columns to rotations of the columns during the growth of the films due to the presence of small open space between the columns, resulting in the porous structure of columns.

On basis of Mg/Pd film, Higuchi *et al.*[83] synthesized 3-layer Pd/Mg/Pd hydrogen storage composite film, which absorbed up to 5.5 mass% H_2 under 0.1 MPa in 24 h at 373 K. By comparing the hydrogen storage capacity of the 2-layer and 3-layer composite films, it was confirmed that the H/Mg ratio in the 3-layer Pd/Mg (800 nm)/Pd film was approximately twice that in the Pd/Mg (800 nm) film, which suggested that coating both sides of Mg film with Pd allows further improving its kinetics. It is believed that the improved hydrogen absorption/desorption properties of the film as a result of double-layer are due to the cooperative effect, the essence of which is elastic interactions between nanostructured Mg and Pd layers: (i) in Pd layer, hydrogen becomes unstable as a result of the catalytic effect of Pd and thereby can be easily released from the upper or lower layer containing at relatively low temperature; (ii) the upper and lower Pd layers exert external pressure on the middle Mg layer, which obviously affects the properties of Mg. Thus, the hydrogen in the Mg layer behaves as in the Pd layer being released below 370 K. This cooperative effect was also observed by other groups.[84] Not only Pd catalyst layer but also the microstructure of Mg layer can improve the kinetics of Pd/Mg/Pd film. Higuchi *et al.*[83] reported that columnar grains in the Mg layer of the Pd/Mg/Pd film were narrower and denser compared with that of in the Mg layer of the Mg/Pd film. Another interesting phenomenon in Pd/Mg/Pd film reported by Higuchi *et al.* was that unlike the Mg/Pd film, the hydrogen desorption temperature of the Pd/Mg/Pd film decreased as the thickness of Mg increased.[83] It is a pity that Higuchi *et al.* did not make an explanation of this phenomenon. In contrast to findings of Higuchi *et al.* about the thickness effect of the Mg layer of the Pd/Mg/Pd thin film on hydrogen storage properties, Qu *et al.*[85] reported that at room temperature, the absorption/desorption kinetics of the Pd/Mg/Pd thin film was improved by reducing the thickness of the Mg layer. As shown in Fig. 1, both hydrogenation and dehydrogenation rates apparently increased when the Mg layer was thinner than 60 nm. Qu *et al.* attributed the thickness effect to the reduction of hydrogen desorption activation energies and the increase of diffusion path for H atoms as well as the negligible blockage of the hydride layer with decrease of the Mg layer thickness down to 60 nm. We tentatively put forward that the difference between research results of Higuchi *et al.* and Qu *et al.* may be due to: (i) in Mg/Pd film, Mg is directly deposited on the substrate of a low temperature, therefore a dense nanocrystal or amorphous structure is formed on the side near the substrate, while a less dense columnar structure is formed on the side away from the substrate. With this in mind, for Mg/Pd film, the thicker the Mg layer, the denser the microstructure of the Mg layer, and then the lower the hydrogen desorption temperature; (ii) the deposition process was continuous in the experiments of Higuchi *et al.*, as a result, the deposition of Mg layer stated before the temperature of the deposited Pd layer was reduced down to the temperature of substrate. As a result, the deposition rate of Mg layer was relatively slow, which leaded to the formation of uniform columnar structure of constant density. Thus, as the thickness of Mg layer increased, the length of the columnar crystal increased, and the grain boundary increased accordingly, which promoted the hydrogen desorption process. It is worth emphasizing that the thickness effect on the microstructure and density of the Mg layer strongly depend on the sputtering parameters, therefore, we believe that the kinetics of the Pd/Mg/Pd film or the Mg/Pd film depending on the thickness of the Mg layer is not unique. However, it can be sure that the kinetics of the Pd/Mg/Pd film is much better than that of the Mg/Pd film.

Compared to bulk Mg, for Pd/Mg/Pd, the enthalpy of formation of MgH_2 is reduced. The reason for the reduction of the enthalpy of formation varies, depending on the particle size of Mg: when the particle size is on the order of 7–9 nm, the grain boundary effects play a leading role, while if the particle size is bigger than the order of 7–9 nm, the effects of excess volume make a main difference.[86]

The Mg deposition method and parameters have a great impact on the hydrogen storage properties of two or more layered Mg/Pd films.[87–92] For example, it was observed that increasing pressures of He effectively allowed better dehydriding properties and the mechanical stability upon cycling. This can be explained that the increasing pressure of He allows on the one hand reduced crystallinity of the Mg layer[92] as well as probably enhanced cooperation effect;[93] on the other hand,

it would induce an extension of the outer Mg/Pd interface region between the Pd and Mg layers, thereby essentially locating hydrogen in Mg phase.[90–94] The extension of the outer Pd/Mg interface region was related to alloying between Pd and Mg layer and/or to the penetration of Pd atoms in the pores of the Mg sublayer.[92]

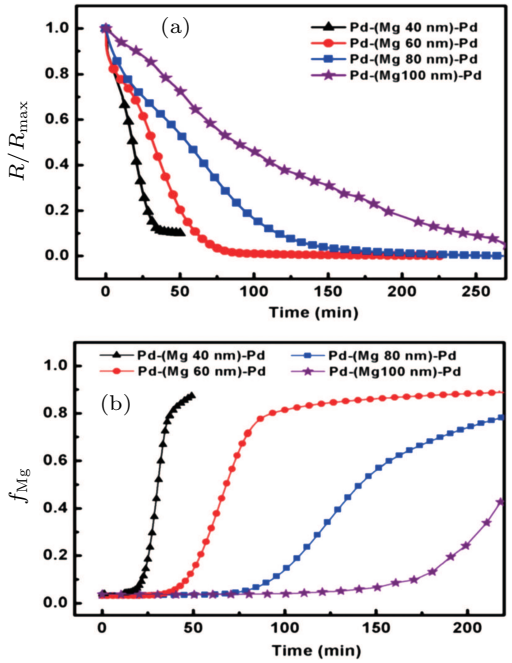


Fig. 1. (a) The relative resistance changes of all the hydride films during dehydrogenation in air at 298 K. R_{max} is the initial resistance of hydride films. (b) The time-dependent volume fractions of Mg, f_{Mg}, of all the hydride films during dehydrogenation in air at 298 K.[85]

Some studies have also shown that hydrogenation properties of the Pd/Mg/Pd system can be significantly enhanced by adding interlayer.[95–98] According to literature reports, there are two ways for adding interlayer into the Pd/Mg/Pd system: (i) interlayer located between the Mg layer and the Pd layer has a catalytic effect as well as a function preventing the formation of Mg_xPd_y intermetallics during the thermal treatments, and allows the hydrogen storage capacity to be increased by inducing the formation of additional hydrogen absorption phases; (ii) when interlayer is located between two Mg layers, only a catalytic effect can be observed. Al is a widely used element for interlayer owing to its ability to improve the thermodynamics of the desorption process.[99] Jain *et al.*[100] prepared Pd (20 nm)/Al (50 nm)/Mg (100 nm)/Pd (20 nm) using vapor deposition method and found that the introduction of Al layer promoted the formation of complex hydride phase $Mg(AlH_4)_2$ along with magnesium hydride, which is responsible for the increase in hydrogen content from 4.34×10^{17} atoms/cm^2 to 6.01×10^{18} atoms/cm^2. In addition, they also proved that the introduction of Al layer can also effectively suppress the formation of Mg_xPd_y intermetallic phase, which exerts negative effect on hydrogenation. Dom'enech-Ferrer *et al.*[101] prepared Pd/Mg/Al/Mg/Pd multilayer film using electron beam physical vapor deposition. They found that the addition of the appropriate amount of Al can promote the hydrogenation of the Mg layer as an activator, thereby improving the hydrogen storage capacity. But they also found that the addition of Al did not significantly reduce the desorption temperature compared to Pd/Mg/Pd films, with a desorption temperature around 403 K–413 K. Jain *et al.*[102] prepared Pd/Mg/Ni/Pd and Pd/Mg/Mg_2Ni/Pd films with the Pd/Mg/Pd base system using vapor deposition and found that Pd/Mg/Ni/Pd and Pd/Mg/Mg_2Ni/Pd films absorb 7.08×10^{17} and 1.68×10^{18} hydrogen atoms/cm^2, respectively, in comparison to 4×10^{17} atoms/cm^2 absorbed by the base system. They contributed the high hydrogen content to the formation of additional hydrogen absorption phase in interlayers of Ni and Mg_2Ni. After adding the interlayer between Mg and Pd layers, Mg_5Pd_2 phase was not generated during hydrogen absorption, which is consistent with the research results of Jain *et al.*[100]

Tan *et al.*[103] investigated the influence of various interlayers (7.5 nm) located between Mg and Pd layers on hydrogen absorption/desorption properties and cycle stability of the Pd (7.5 nm)/Mg (1.5 μm)/Pd (7.5 nm) thin film system at 523 K. It was observed that from the third cycle, the catalytic effect of Pd/Nb and Pd/Ti on both absorption and desorption begins to stabilize. In spite of a two times higher value of the steady desorption time in Pd/Ta than in Pd/Nb and Pd/Ti, it is worth noting that samples with the Pd/Ta catalytic layers showed a more steady absorption behavior with the number of cycles increasing. Despite having very rapid initial sorption rates, the composite with the Pd/Fe bi-layer cannot be cycled beyond the first adsorption/desorption. No confirmed explanation of the effect of different interlayers on the hydrogen absorption/desorption properties was not offered by Tan *et al.*

Like in the Pd/Mg/Pd sandwich film, adding interlayer into Mg/Pd multilayer film as well allows for greatly improved hydrogen absorption/desorption properties of the original system. Jung *et al.*[104] investigated the microstructure and hydrogen storage properties of a 60-layer film of Pd (40 nm)/Ti(x nm)/Mg (360 nm)/Ti (x nm) (x = 10, 20, 30, 40, and 50) using an ultra-high vacuum DC magnetron sputtering system. The highest hydrogen absorption capacity of the Pd/Ti/Mg/Ti film was 4.46 mass% for $x = 50$. The hydrogen absorption rate accelerated remarkably with increased thickness of the Ti layer, from 209 min for $x = 10$ to 39 min for $x = 40$. These results demonstrate that the Ti layer in the Pd/Ti/Mg/Ti films serves as a blocking layer, preventing the formation of Mg–Pd intermetallic phases and provides additional diffusion paths for hydrogen atoms, which leads to enhanced hydrogen storage properties. The positive effect of Ti interlayer was also confirmed by Jung *et al.*[105] and Reddy *et al.*[106]

Fry *et al.*[107] compared 150-layer Pd/Mg/Pd film with interlayers of Cr and V respectively. It was found that the chromium-catalyzed coating had the most favorable hydrogen storage kinetics with an activation energy for the dehydrogenation reaction of 65.7 ± 2.5 kJ·mol^{-1}, which was reduced by 70 kJ·mol^{-1} compared with Pd/Mg/Pd multilayer film without transition metal interlayers. Besides, 6.1 ± 0.3 mass% was achieved at around 573 K. Furthermore, Fry *et al.*,[108] changing the pure transition metal interlayer into a mixture of transition metals (TM) rich in Ni (target purity 99.99%) with additions of Fe and Cr, obtained Pd/Mg/Pd multilayer with hydrogen storage properties similar to Ref. [107]. It was observed that hydrogenation of the thin film took place within minutes at 563 K with a reversible capacity of 4.6 mass% and the activation energy of the dehydrogenation reaction was calculated to be 71.6 kJ·mol^{-1}.

The hydrogen storage properties of Mg/Pd film added with Fe interlayer[109] and Nb interlayer[110] have also been reported in literatures and have been improved to varying degrees in different aspects.

3.1.3. Non-palladium capped Mg film

In general, the Mg/Pd film has better hydrogen absorption/desorption kinetics, but the price of Pd is too high that it is difficult to realize large-scale applications of Mg/Pd film. Therefore, the research on non-palladium capped Mg film appears. The studies of Ouyang *et al.*[39,111–113] are representative in terms of Mg/(rare earth alloy) multilayer films. They reported that for nine-layer Mg/Mm–Ni (Mm denotes La rich rare earth alloy) multilayer film, the hydriding and dehydriding temperatures of Mg layers in the Mg/Mm-Ni multilayer film were remarkably decreased that the hydrogen absorption and desorption started at 373 K and 473 K, respectively. Ouyang *et al.* attributed the improvement of the hydrogen storage properties of Mg to the catalytic roles of the Nd(La)Ni_3 existing in the Mm–Ni layer and Mg_2Ni phases existing in the interfacial regions between the Mg and Mm–Ni layers.[111] They also reported that in MmM_5/Mg (here, Mm denotes mischmetal, MmM_5 denotes $MmNi_{3.5}(CoAlMn)_{1.5}$) multilayer thin films, the absorbed hydrogen can be fully released at 523 K. In addition, they explained the improvement of hydrogen absorption/desorption properties of the film system in terms of the microstructural characteristics of MmM_5 and Mg layers.[39,112] The MmM_5 layers consisted of two kinds of structures: an amorphous structure with a thickness of ~ 4 nm grown at the bottom of the layers, on which a randomly orientated nanocrystallite structure was formed. Unlike the MmM_5 layers, the Mg layers were composed of columnar crystallite with [001] direction nearly parallel to the growth direction. The reason for the formation of amorphous, nanocrystalline, and columnar structures can be referred to Section 3.1.1 or literature,[113] in which Ouyang *et al.* gave a very detailed explanation. When the film starts to absorb hydrogen, the MmM_5 layer on the surface of the film easily absorbs hydrogen due to that the hydrogen absorption kinetics of MmM_5 is splendid. Then, the hydrogenation of Mg, which is adjacent to the MmM_5 layer, is able to be easily completed due to the catalytic effect of the MmM_5 phase on the hydrogenation process of Mg[114] or "cooperative phenomena".[83,84,115] Furthermore, a fast diffusion of hydrogen into the interior of the Mg layer can be achieved owing to many hydrogen diffusion channels provided by the boundaries distributed between the columnar crystallites of Mg. It is worth emphasizing that the hydrogen diffusion through the closest packed plane of Mg could be avoided due to the gateway, which is provided by the diffusion channels and through which hydrogen could diffuse along the substrate plane of Mg, close packed (001) plane. Therefore, the improvement of hydrogenation kinetics of Mg could be achieved. The explanation of improving diffusion and reaction kinetics given above is valid as well as for the dehydrogenation reaction since dehydrogenation is the reverse process of hydrogenation. It is noteworthy that unlike Mg/Pd film, in MmM_5/Mg film, interface phases are not observed in all interfaces between different layers.

Mn-capped,[116] Pt-capped,[117] and Cu-capped[118] Mg films have also been reported in literatures. Especially in the Mg/Cu multilayer film prepared by Akyildiz *et al.*,[118] the Mg phase could be converted totally into MgH_2 at temperatures not greater than 473 K; however, when hydrogenation occurred above 473 K, some Cu still diffused into the Mg layer to form Mg_2Cu intermetallic, which inhibited hydrogenation of Mg. In recent years, a new type of Mg thin film system appears, i.e., the Mg/polymer thin film. Studies have shown that a polymer coating at the surface of Mg film facilitated the uptake and release of hydrogen in Mg at low temperatures below 423 K (at high temperatures, the polymer will decompose) as well as being an effective way to protect the underneath Mg film against oxidation owing to the low oxygen and water permeability, and no significant oxidation was observed after exposing film to air for one week.[119] In addition, polymer layer significantly improved the possibility of the Mg layer remaining hydrogen in the film exposed to air that the hydrogen storage capacity could be remained after a few hours,[120] even after one week of exposure to air.[119] However, it is worth emphasizing that polymer may greatly reduce the hydrogen storage capacity of the film.[121]

3.2. Mg alloy films

Among Mg-based hydrogen storage alloys, Mg–Ni hydrogen storage alloys are the most studied ones, which not only have relatively high hydrogen storage capacity, but also have better activity of hydrogen absorption/desorption. Therefore, Mg–Ni alloy film is the most studied among all kinds of

Mg alloy films.[122–126] Ouyang *et al.*[127–129] reported hydrogen storage properties of multilayer Mg–Ni thin film capped with Pd or MmM_5. For MgNi/Pd multilayer with the total thickness of 1.7 μm, the hydrogen absorption content reached 4.6 mass% at room temperature and the hydrogen desorption reached 3.4 mass%.[127] For $Mg_{2.9}Ni$/MmM_5 multilayer, a maximum hydrogen absorption content of 5.0 mass% was achieved. However, the hydrogenation properties were deteriorated after 5 hydriding/dehydriding cycles. Ouyang *et al.* attributed it to the volume expansion and shrinkage of MmM_5 layer as well as the poor binding force between the $Mg_{2.9}Ni$ layer and MmM_5 layer, which consequently leaded to full peeling of the MmM_5 layer from the $Mg_{2.9}Ni$ layer, thereby disabling the catalytic role of MmM_5 layer, leading to the deterioration of hydrogenation properties of $Mg_{2.9}Ni$/MmM_5 multilayer film.[128]

It is worth noting in all practical uses that even minute impurity levels of oxygen and water can result in the formation of thin oxide barrier film on the surface of Mg alloy film.[130–132] Wirth *et al.*[130] developed the hydrogen uptake mechanism depending on the thin oxide film by investigating characteristics of dependence of the hydrogen storage capacity and oxygen content in the Mg–Ni (1.5 μm)/Ni (5 nm) film on hydrogen absorption time and hydrogen absorption temperature (Fig. 2). They believed that the fact that hydrogen atoms can pass through the oxygen barrier layer is due to the diffusion of hydrogen atoms as well as pinholes or defects in the oxide layer, which allows a much smaller activation energy than for oxide films with a continuous structure. As shown in Fig. 2, L is the mean distance between defects, which plays a role of channels for hydrogen transport through the barrier oxide layer, and λ denotes the mean surface diffusion length of an adsorbed hydrogen atom. In the case of $L \gg \lambda$, the processes of hydrogen diffusion and desorption prevail over the hydrogen trapping by defects. Upon further hydrogenation, a modification of the Mg_2Ni structure occurs, generating the microcracks and leading to the increase of the density of defects on the surface, thereby $\lambda > L$, so that dominant processes transform from hydrogen diffusion to the hydrogen trapping by defects in the organization of hydrogen transport from the surface into the bulk (Fig. 2(c)). Based on this, Wirth *et al.* put forward two factors influencing hydrogen permeability: (1) the increase of thickness of the oxygen barrier layer leads to the decrease of hydrogen permeability, and (2) the increase of density of surface defects allows increased hydrogen permeability through the oxygen barrier layer. Furthermore, they believed that hydrogenation is achieved by three steps: (1) the initial step is associated with diffusion of hydrogen through the growing thin oxide barrier film; (2) the second step is a transient period, when dynamic stresses are generated as a result of the formation of hydrides in the bulk of film material and a flexible surface topography is formed with defects and cracks in the oxide barrier layer, which becomes new hydrogen transport paths through the barrier layer; (3) the last step is the steady state hydrogenation after stabilization of surface topography adjusted to the hydrogen uptake rate, which is adapted to the hydrogenation parameters and properties of material.

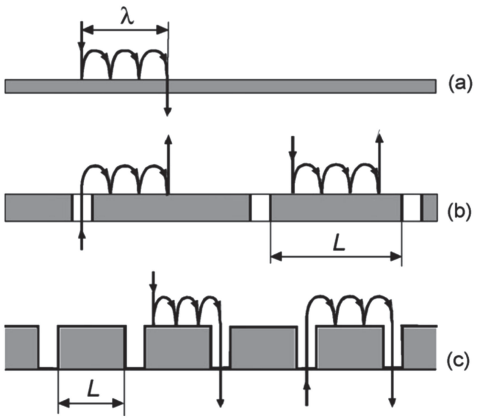


Fig. 2. The schematic illustration of hydrogen transport through the barrier layer.[130]

Among all the 3d metal elements, the catalytic performance of Nd is significantly higher than other elements, and its addition can greatly accelerate the hydrogen absorption/desorption reaction on the surface of Mg; in addition, its price is relatively low. Mosaner *et al.*[133] studied the structure and hydrogen absorption/desorption properties of Mg–Nb thin film and found that the Mg–Nb film obtained by vapor deposition showed two structures: a uniform thin layer with a thickness of approximately 1 μm and a surface with spherical grooves. The study showed that the diameter of the spherical groove was related to the sputtering current density: the diameter of the spherical groove obtained under low current density was less than 2 μm while the groove diameter obtained under high current density was more than 10 μm. Comparing the hydrogen absorption/desorption properties of Mg–Nb film and pure Mg film, it was found that the Mg–Nb film had a higher hydrogen absorption activity and could desorb at a relatively low temperature. This could be explained that the element Nb was uniformly dispersed in the thin film structure in the form of nanoclusters and became the activation center of hydrogen, thereby accelerating the hydrogen desorption, which suggested that the formation of nanoparticles or nanostructures plays a key role in improving the hydrogen absorption/desorption properties of Mg. Huang *et al.*[134] reported that compared with Pd-capped Mg (100 nm)/Nb (10 nm) eight-layer film, for Pd-capped Mg-10 at% Nb alloy film with a similar Mg to Nb atomic ratio, the initial hydrogen desorption temperature was reduced by 5 K and the peak temperature of hydrogen desorption was reduced by 10 K. This subtle difference was related to smaller grain of Mg as well as more uniform distribution of Nb in Mg-10 at% Nb alloy film, which along with small clusters provided more nucleation sites for

MgH_2/Mg and channels for H diffusion. The role of Nb and small clusters as nucleation sites has also been reported by Checchetto *et al.*[135] and Mengucci *et al.*[136]

The Mg–A1 hydrogen storage alloy has the advantages of high hydrogen storage capacity and low cost, which determines the possibility of its use in the form of thin film to improve its hydrogen storage properties. Pranevicus *et al.*[137] synthesized a MgAl film with a thickness of about 3 μm to 5 μm using PVD method. The composition of the film was determined as $Mg_{17}Al_2$ by x-ray diffraction (XRD) analysis, which was consistent with the Mg–Al binary phase diagram, where Al has a limit solubility of 4.5% in Mg. After the film was hydrogenated by hydrogen plasma at 303 K for 30 min, it gradually changed to $Mg(AlH_4)_2$, which corresponded to the absorption of 9.3 mass% hydrogen. This is unmatched by any other type of hydrogen storage alloy. The structure of the obtained film was greatly affected by the ion sputtering intensity, when the ion sputtering intensity increased from 0.05 nm/cm^2 to 0.1 nm/cm^2, the grain size of the film decreased rapidly from 40 nm $\sim$ 50 nm to 20 nm $\sim$ 30 nm, and the hydrogen kinetics was also greatly improved, which suggested that high sputtering intensity facilitates the activity of the film. However, to completely release hydrogen from the film, the temperature needs to be raised up to above 483 K, as a result, a new phase Al_2Mg_3 will be generated, which will destroy the reversible hydrogen absorption/desorption properties of the film, thereby shortening the life of the film.

High hydrogen storage capacity and fast hydrogen desorption rate of the Mg–Sc alloy thin film were reported by Niessen *et al.*[138–140] They investigated the electrochemical hydrogen storage properties of Mg_xSc_{1-x} alloy films and found that $Mg_{80}Sc_{20}$ had the maximum capacity of 6.5 mass%, which was 0.9 mass% bigger than that of bulk materials due to shorter diffusion lengths. In addition, based on the comparation of hydrogen storage properties of $Mg_{80}X_{20}$ (X = Sc, Ti, V, Cr) compound thin films, they proved that the hydrogen storage capacity and faster hydrogen desorption rate resulting from Sc alloying are higher than those resulting from Ti, V, and Cr alloying.

Mg–C,[141,142] Mg–Fe,[143,144] Mg–Pd,[145] Mg–Ti,[55,146–148] Mg–Co,[149] and ternary Mg alloy films[150–153] have also been reported in literatures. These Mg alloy films all improve the hydrogen storage properties to varying degrees compared with bulk materials and pure Mg film.

4. Summary

After the commercialization of hydrogen storage materials, the requirements for low cost and high performance make the preparation methods more diversified. The preparation of Mg-based hydrogen storage materials in the form of thin films can effectively control the microstructure of the material and obtain amorphous and nanocrystalline hydrogen storage alloys with good hydrogen absorption/desorption activity.

Mg-based thin films have attracted much attention not only because Mg-based thin films can be used to store hydrogen, but also because the preparation of Mg-based thin film materials as electrodes, in spite of their poor electrocatalytic properties, can promote the development of magnesium or Li-ion batteries. In addition, Mg-based films can also be used as optical/electrical sensors as a result of the changes in electronic state via a metal-isolator transition which takes place during the hydrogenation of magnesium films.

To improve the hydrogen absorption/desorption properties of Mg, the currently prepared Mg-based films generally need to use high-priced Pd as a catalytic component, which generally results in the formation of Mg–Pd intermetallics, weakening the catalytic effect of Pd. In addition, notwithstanding using interlayer and developing non-palladium capped Mg film allows the hydrogen storage properties to be improved to a certain degree, but it is still not meeting the needs of practical application. Furthermore, for both Pd-capped Mg film and non-palladium capped Mg film, a narrow temperature interval for effective hydrogenation is always observed. At temperatures below this interval, the hydrogen sorption rate is slow, whereas at temperatures above the interval, the internal reaction is dominant so the intermetallics dominate the structure. Unless the intermetallics absorb hydrogen (for example, intermetallic Mg_2Ni formed in interlayers of Pd/Ni/Mg/Pd film as reported in Ref. [63]), employing the high hydrogenation temperatures does not make much sense. Although alloying Mg film with other elements can also improve hydrogen storage properties in some aspects, but the effect is single, usually achieved by sacrificing hydrogen storage properties in other aspects. This has been the case for current Mg film systems. Besides, the influence of microstructure of film system on the hydrogenation/dehydrogenation mechanism and properties is still controversial.

According to current literatures, we tentatively put forward that: (1) in the case where the total grain boundary area is constant, the greater the density, the more grains per unit distance in the free path of the hydrogen atom, and the more hydrogen atom–grain reaction occurs, thereby the hydrogen absorption/desorption properties are facilitated; (2) in the case where the degree of density is constant, the larger the total grain boundary area, the more the diffusion channels, and the better the hydrogen absorption/desorption properties; (3) a highly oriented columnar structure may promote hydrogen absorption/desorption. In view of the current research status and development trends, we believe that there are three key research directions in the future: (1) looking for a cheap metal element to replace the high-priced Pd to coat Mg film for catalyzing hydrogen absorption/desorption as well as preventing oxidation of Mg film; (2) compositing Mg film with

other hydrogen storage alloy of catalytic elements to obtain Mg-based alloy thin films with excellent kinetics; (3) the research of influence of film preparation method and parameters on the microstructure of film system followed by the research of influence of microstructure of film system on hydrogenation/dehydrogenation mechanism and properties in order to realize accurate computer design of Mg-based film systems with expected hydrogen storage properties.

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