Rare Metal Materials and Engineering
Volume 50, Issue 6, June 2021
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Zhao Yunsong, Zhang Mai, Guo Yuanyuan, et al. Review on Hydrogen Storage Property and Preparation of Nanostructured Mg[J]. Rare Metal Materials and Engineering, 2021, 50(06): 1999-2007.

REVIEW

Review on Hydrogen Storage Property and Preparation of Nanostructured Mg

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Abstract: The utilization of hydrogen energy has attracted great attention, while the storage and transportation of hydrogen restrict its wide practical application. As a solid hydrogen storage material, Mg-based alloys show great potential in the field of hydrogen storage. However, the high temperature of hydrogen absorption and release, and the slow rate of hydrogen release cast a shadow on its engineering application. To improve the hydrogen storage capacity of Mg-based alloys, the researches mainly focus on the optimization of alloy composition and the improvement of processing technology, and nano refinement is one of the most promising methods. In this study, all the processing technologies of nanostructured Mg are introduced, including high energy ball milling, physical vapor deposition, hydriding chemical vapor deposition, liquid-phase chemical synthesis and template method. The advantages and disadvantages of each method are also analyzed. The effect of nanostructure and element doping on the hydrogen storage property of Mg-based alloys is summarized. This study provides a reference for the research of the material development and improvement of preparation technology in hydrogen storage field.

Key words: hydrogen energy; Mg-based alloys; nano refinement; hydrogen storage property; hydrogen desorption performance

Energy plays an important role in social operation and sustainable development. At present, non-renewable energy such as oil, coal and natural gas are still the main energy sources. However, the gradual depletion of these fossil fuels and the environmental pollution issues drive human to consider the adjustment of energy structure, and promote the development and utilization of environment-friendly renewable clean energy. Fig. 1 shows the evolution of the world total primary energy supply and the world population supported by the earth ecosystem[1]. Renewable energy will gradually replace the traditional fossil fuel, and its share in the energy structure gradually increases. Around 2050, all energy sources will be renewable and are mainly in the forms of batteries and hydrogen. There is no doubt that the development and utilization of hydrogen energy will be crucial in the future.

Hydrogen energy has three typical advantages when

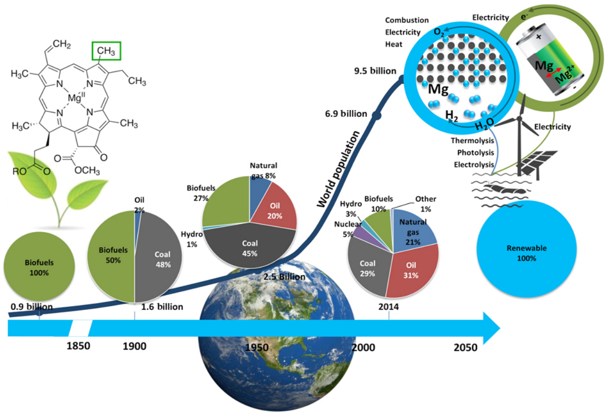

Fig.1 Evolution of the world total primary energy supply and the world population supported by the earth ecosystem[1]

Received date: August 22, 2020
Foundation item: National Natural Science Foundation of China (91860202)

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compared with the traditional fossil fuels: wider source (the product of water electrolysis), higher combustion value and more environmentally friendly (the reaction product is water). This makes hydrogen energy one of the most potential renewable energy sources to replace the fossil energies. Production, application, storage and transportation are all important for the development and utilization of hydrogen energy, and hydrogen storage has become the main technical bottleneck restricting the wide application of hydrogen energy.

Up to now, the most mature technology for hydrogen storage is high-pressure steel cylinders, that is, to liquefy hydrogen into liquid and store it in the cylinders. However, this storage technology is restricted by the withstand pressure of the cylinders, and there is a risk of hydrogen overflow. Moreover, the upper limit of hydrogen storage efficiency is as low as 0.1wt%. This drives the development of new hydrogen storage technologies and solid hydrogen storage technology show a promising application prospect. The solid hydrogen storage materials usually achieve the purpose of hydrogen storage by reversible reaction with H_2. Fig. 2 is the schematic diagram of the catalytic mechanism of nonstoichiometric TiC_x during the hydrogenation and dehydrogenation processes of the Mg-TiC_x@C nanocomposites[2]. Mg particles react with H_2 to form MgH_2 during the hydrogenation process, and the product MgH_2 decomposes to Mg and H_2 during the dehydrogenation process. As a catalyst, TiC_x accelerates the hydrogenation and dehydrogenation processes.

Solid hydrogen storage materials mainly include physical adsorption materials, metal-based hydrogen storage alloys and composite hydrogen storage materials[3]. Based on the alloy composition, metal hydrogen storage materials can be divided into Mg-based, rare earth-based and Ti-based hydrogen storage materials. Mg has a reversible hydrogen storage capacity (7.6wt%), low density (1.73 g/cm^3), abundant reserves (the 8th richest element in the crust) and low price. More importantly, the hydrogen storage capacity of Mg reaches 7.6wt% . This makes Mg-based alloys the most promising solid hydrogen storage material. Fig. 3 shows the gravimetric hydrogen capacity and sorption temperature of various hydrogen storage materials[4]. The result indicates that the hydrogen storage performance of Mg hydrides is significantly higher than that of chemical hydrogen and adsorbents.

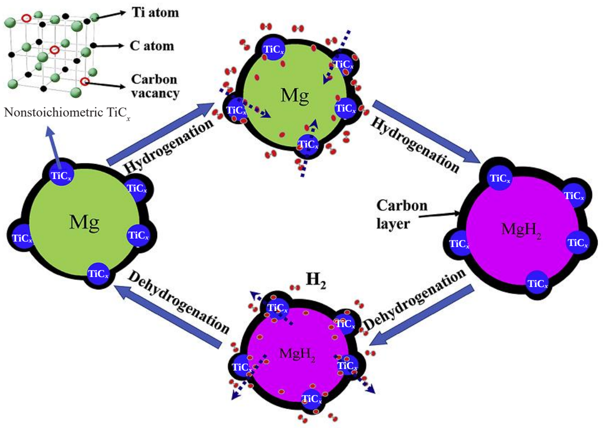

Fig.2 Schematic diagram of the catalytic mechanism of nonstoichiometric TiC_x during the hydrogenation and dehydrogenation processes of the Mg-TiC_x@C nanocomposites[2]

It is worth noting that the practical application of Mg-based hydrogen storage alloys faces two thorny problems: high hydrogen absorption and desorption temperature (nearly 300 °C), and low hydrogen desorption rate. Therefore, multiple methods such as adjusting the alloy composition, developing new processing technology and modifying the alloy surface state, are used to improve the hydrogen storage capacity. Studies have shown that reducing the diameter of Mg to a nanometer level can effectively improve the kinetics[2] and thermodynamics[5] of hydrogen absorption and desorption. In addition, nano refinement of Mg has been proved to be one of the most effective ways to improve the hydrogen storage capacity of Mg-based alloys. This study introduces the processing technology and hydrogen storage property of nanostructured Mg-based alloys.

1 Preparation Technologies of Mg Nanostructures

The aim of preparation technology is to obtain Mg particles with the smallest size as possible and element doping in the preparation process. At present, there are five preparation technologies, namely high energy ball milling, physical vapor deposition, hydriding chemical vapor deposition, liquid-phase chemical synthesis and template method.

1.1 High energy ball milling

High energy ball milling (HEBM) is one of the most widely used methods to prepare Mg nanoparticles[6,7]. Fig. 4a illustrates the schematic diagram of HEBM method. Nanostructure materials are obtained by reducing the material size to nanometer level through physical grinding. Zaluska et al[8] used Mg powder as raw material and milled it for 20 h to get Mg nanoparticles, as shown in Fig.4b, in which various nanoparticles with the size of 20~30 nm exist. Fahimpour et al[9] also prepared nanoscale Mg particles and MgH_2 particles

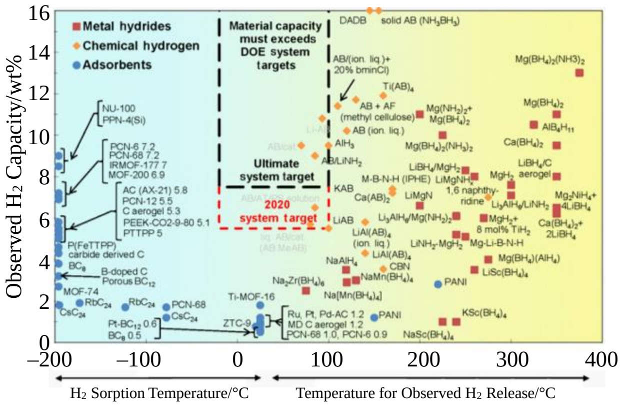

Fig.3 Gravimetric hydrogen capacity and sorption temperature of various hydrogen storage materials[4]

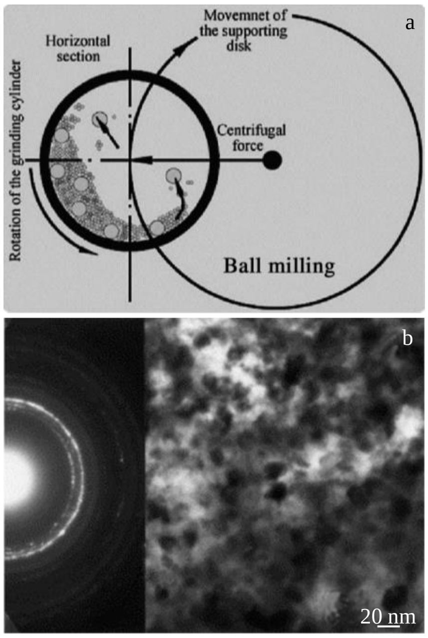

Fig.4 Schematic diagram of HEBM method[10] (a) and TEM image[8] (b) of Mg nanostructure

using this method. This implies that ball milling is an effective way to prepare Mg nanoparticles.

HEBM method can also be used to prepare Mg-based alloy materials and dope nano materials. A series of research attempts to change the compositions of nanostructure Mg particles by doping, so as to improve their hydrogen storage performance. Zaluska et al[8] doped Mg nanocrystals with various elements including Pd, Li, Al, Ti, V, Mn, Zr, Y, etc. Khan[11] prepared 2MgH_2-Co powder by milling MgH_2 and Co powders in the molar ratio of 2:1. In addition to the doping of pure metal, Cr_2O_3, Nb_2O_5, $LaNi_5$[12], TiCu[5] and TiCr can also be doped in Mg/MgH_2 nanocrystals by HEBM method[13].

In conclusion, the HEBM method has the advantages of simple operation, high controllability and multiple functions. However, the HEBM method usually requires a long preparation time, impurities are thus easily introduced and Mg is easily oxidized. Moreover, it is difficult to refine the product to a size smaller than 100 nm by HEBM method due to the excellent ductility of Mg. As a result, the resulting nanoparticles are usually encapsulated in a large micron sized particle.

1.2 Physical vapor deposition

Physical vapor deposition (PVD) is also a mature and widely used method to prepare nano materials. In this method, solid or liquid materials are heated or bombarded by high-energy beams (electrons, atoms or ions, etc) to evaporate into a gaseous state, and then deposited on the substrate to form nanomaterials. In comparison with the HEBM method, the products prepared by PVD methods have the following advantages: (1) smaller size, (2) higher purity, (3) more diversified morphologies, and (4) more easily modified by doping.

The PVD methods for the preparation of nanostructured Mg can be subdivided into the inert gas condensation (IGC), the plasma metal reaction (PMR), the glancing angle deposition (GLAD) and the vapor transport (VT) methods. The differences between the above methods are mainly located in energy source, environmental atmosphere and preparation angle, thus leading to different morphologies of nanostructured Mg. Fig. 5 depicts the schematic diagram of the ultra-high vacuum (UHV) compatible system of the IGC method[14], where inert gas is injected to prepare the raw materials during the preparation process[15]. Mg nanoclusters can be produced by dc magnetron sputtering and inert gas condensation inside an UHV[16].

Fig.6 shows the schematic diagram for the formation of the Mg-TiC_x@C nanocomposite by plasma metal reaction (PMR) method[2]. Plasma arc was generated to evaporate the source materials to prepare nanoparticle materials. Liu[17] and Hu[2] prepared Mg-V, Mg-La-Al, Mg-La-Ni and Mg-TiC_x@C composite nanoparticles by controlling the content of alloying elements in the evaporation source by the PMR method. Fig. 7a is the schematic diagram of GLAD method, and nano materials are prepared by a large angle inclined deposition during processing[18]. Different from traditional electron beam evaporation method, the vapor flow is not perpendicular to the substrate, but placed with a larger angle, usually 70°~90°. The morphology of nanostructured Mg is always in the form of sheets, as shown in Fig. 7b[19]. Various elements such as Ti[20], Pd[21] and V[22] have been successfully doped in Mg nanosheets by the GLAD method.

1.3 Hydriding chemical vapor deposition

Fig. 8 illustrates the schematic diagram of hydrating chemical vapor deposition (HCVD) method[23]. This method is firstly developed by Zhu[24] to prepare Mg nanostructures. Mg in solid state is evaporated in H_2 atmosphere under the pressure of 1~6 MPa at 600 °C. Single crystal MgH_2 nano-wires are

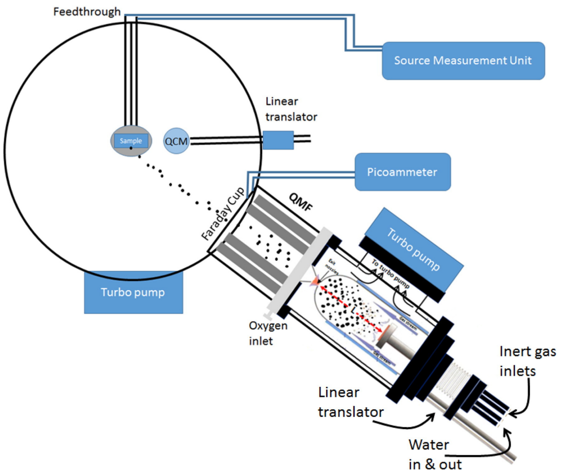

Fig.5 Schematic diagram of the ultra-high vacuum (UHV) compatible system[14]

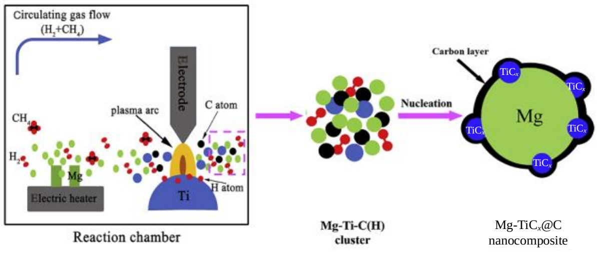

Fig.6 Schematic diagram for the formation of the Mg-TiC_x@C nanocomposite using plasma metal reaction (PMR) method[2]

obtained by hydrogenation on a water-cooled low-temperature substrate and the crystallinity is higher than that obtained by hydrogenated bulk Mg. H_2 pressure has a strong driving force in the preparation of MgH_2 nanowires, and a high H_2 pressure contributes to the preparation of the products with a small diameter and a linear shape.

1.4 Liquid-phase chemical synthesis

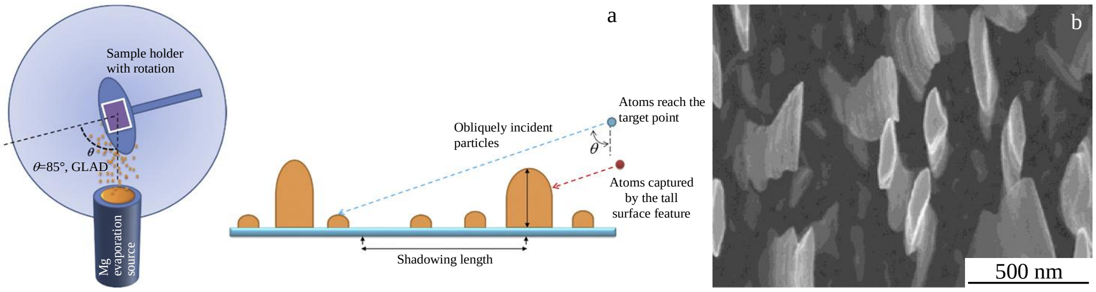

Fig.7 Schematic diagram of GLAD[18] (a) and SEM image[19] (b) of Mg nanosheets

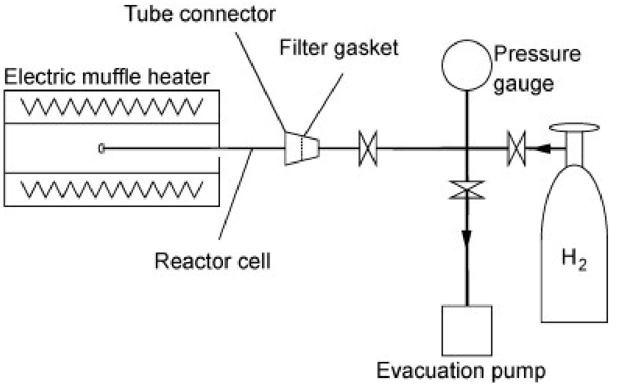

Fig.8 Schematic diagram of hydrating chemical vapor deposition (HCVD) method[23]

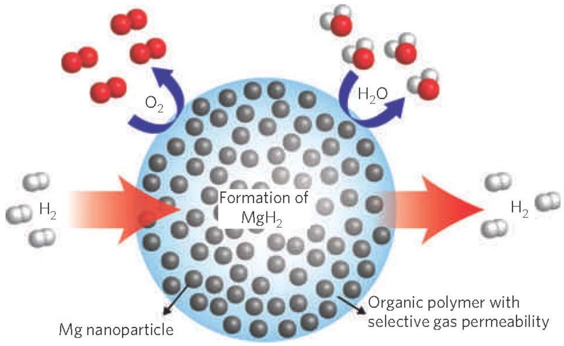

Fig.9 Schematic diagram of liquid-phase chemical synthesis method[25]

The method of liquid phase chemical synthesis uses liquid-phase chemical reactions to prepare nanoparticles, and it can be divided into liquid-phase chemical reduction method and liquid-phase chemical decomposition method. Fig.9 shows the schematic diagram of liquid-phase chemical synthesis method[25]. Mg nanoparticles are synthesized using the liquid-phase chemical reduction method through electrochemical reduction or chemical replacement reaction. In general, Mg nanoparticles are prepared by reduction and oxidation reactions in a tetrahydrofuran (THF) solution[26]. In addition, Mg nanoparticles can also be prepared by decomposing compounds containing Mg, that is, the method of liquid-phase chemical decomposition. Setijadi et al[27] prepared nanostructured MgH_2 by decomposing $MgBu_2$ in vacuum or solution by thermal decomposition method. The difference is that MgH_2 is rod-shaped when it is prepared in vacuum, but scale-shaped or rounded in a solution.

Nano Mg particles with a small size and uniform particle size distribution can be prepared by liquid-phase chemical synthesis. However, the preparation process of this method is tedious, and the reaction rate is slow and lasts for a long time. Moreover, products usually contain impurities, such as solution residues and by-products, which are difficult to remove completely.

1.5 Template method

The template method takes the materials with nano pores as the skeleton, and then fills the materials into these pores. As the pore size is controlled in a nano size, the size of the filler is also limited to nano scale. Mg and MgH_2 nanoparticles have been successfully prepared by this method[28]. Fig. 10 is the schematics displaying the self-assembled MgH_2 on three-dimensional metal interacted carbon[29]. Mg nanoparticles are prepared by 3-D carbon coordinated transition metal cations as a template. This method can directly control the size of nanoparticles by controlling the size of the skeleton hole, but it also leads to the problem that the skeleton cannot be removed.

The size and shape of the products, as well as the advantages and disadvantages of the above five preparation methods are summarized and listed in Table 1. The size of products obtained by high energy ball milling, physical vapor deposition and hydriding chemical vapor deposition methods are tens of nanometers, which is larger than that produced by liquid-phase chemical synthesis and template methods. Each preparation method has a corresponding product shape, mainly including nanoparticles, nanoclusters, nanowires and sheets. The characteristics of preparation process lead to different advantages and disadvantages, as shown in Table 1.

2 Hydrogen Storage Properties of Mg Nanostructures

2.1 Effect of nanocrystallization on the storage capacity of hydrogen absorption and desorption of Mg

All the studies have shown that the hydrogen storage performance of pure and element doped Mg nanoparticles is significantly improved compared with that of large-scale Mg metal. Fig. 11 shows the hydrogen absorption curves of Mg grains in different sizes[8]. When the size of Mg particle decreases from a micron level to a nanometer level, the hydrogen storage capacity is improved significantly. The hydrogen storage capacity continues to increase when Mg particle size decreases from 50 nm to 30 nm. Obviously, the hydrogen storage property of Mg can be enhanced by nano refinement.

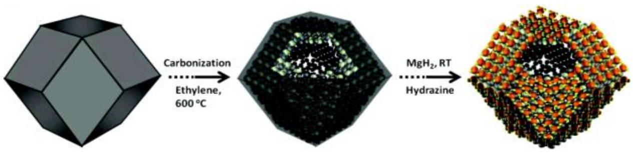

Fig.10 Schematics displaying the self-assembled MgH_2 on three-dimensional metal interacted carbon[29]

Nano refinement can also improve the adsorption and release kinetics of hydrogen in Mg-based materials. When the size of TiC_x-decorated Mg nanoparticles is limited to 2~3 nm, the synergistic effect of carbon confined nanostructures and the catalytic effect of nonstoichiometric TiC_x modified on magnesium nanoparticles significantly enhance the hydrogen storage kinetics[4]. Galeya et al[30] also found that when Ni is added to the surface of Mg/MgH_2 system, the hydrogen storage performance of the composite is significantly improved in comparison with pure milled MgH_2, and the highly dispersed Ni has a positive impact on the kinetics and thermodynamics.

Fig. 12 depicts the schematic diagram of graphene-encapsulated/Mg nanocomposite[31], and an atomically thin oxide layer exists at the interface between Mg nanoparticles and graphene encapsulation. The outermost atomic layer of Mg is slightly oxidized to form a monolayer of honeycomb MgO, which is beneficial for the hydrogenation kinetics. In addition, the combination of nano doping and alloying can also improve the hydrogen storage performance. Fig.13 shows the con-ceptual model of an MgH_2 nanocluster and the distribution of nano catalyst over the active surface sites for efficient hydrogen storages[32]. The collision frequency between H_2 molecules and transition metal nanoparticles increases with decreasing the catalyst size, and the activation barrier can be drastically reduced by nano catalyst doping,

Table 1 Size and shape of products as well as the advantages and disadvantages of different preparation methods

Method	Size of products	Shape of products	Advantages	Disadvantages
High energy ball milling	Tens of nanometers	Nanoparticles	(1) simple operation (2) high controllability (3) multiple functions	(1) long duration (2) impurities are easily introduced (3) Mg is easily oxidized
Physical vapor deposition	Tens of nanometers	Nanoclusters (IGC), nanoparticles (PMR), sheets (GLAD), and nanowires (VT)	(1) small size (2) higher purity (3) more diversified morphologies (4) easily modified by doping	Bombardment of high-energy ions may destroy the basement structure
Hydriding chemical vapor deposition	Tens of nanometers	Nanowires	Rate-limiting step in the solid-gas reaction are removed	(1) specialty equipment (2) complicated process
Liquid-phase chemical synthesis	<10 nm	Nanoparticles	(1) small size (2) uniform particle size distribution	(1) tedious process (2) slow speed rate (3) long duration (4) impurities are difficult to remove
Template method	<10 nm	Nanoparticles	Controllable size	Skeleton can’t be removed

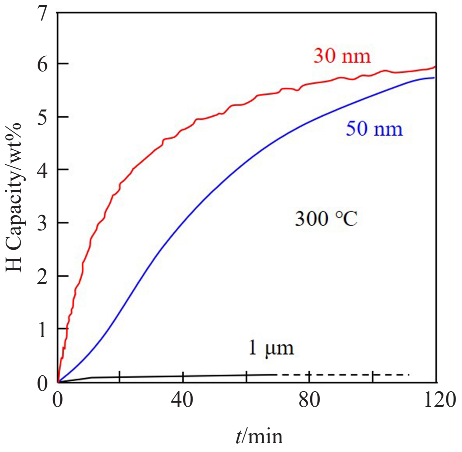

Fig.11 Hydrogen absorption curves of Mg grains with different sizes[8]

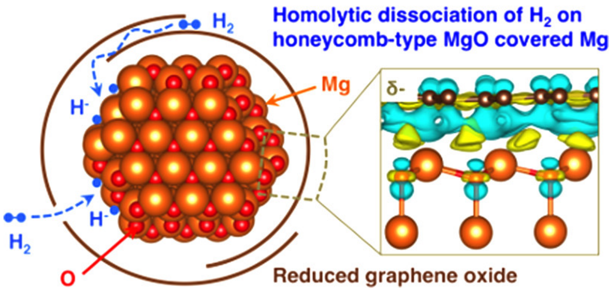

Fig.12 Schematic diagram of Graphene-encapsulated/Mg nanocomposite[31].

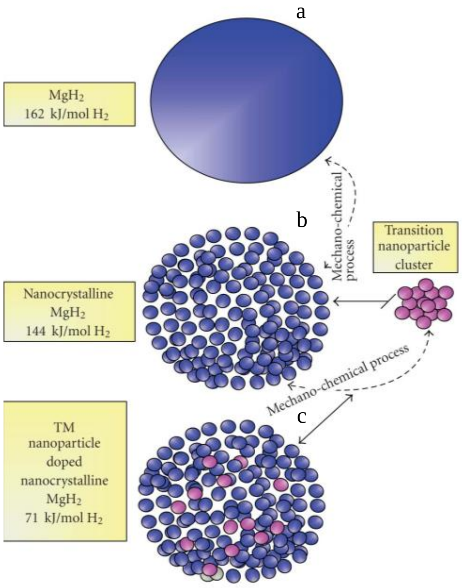

Fig.13 Conceptual model of MgH_2 cluster: (a) plain, (b) nanocrystalline, and (c) nanocatalyst-doped materials[32]

thus improving the activation performance.

Generally, doping plays a positive role in improving the dynamic properties of Mg nanoparticles. Liu et al[33] showed that the initial dehydrogenation temperature of Mg nanoparticles decreases by 94.3 °C after doping with Pd. Other elements including Li, Al, Ti, V, Mn, Zr and Y can also improve the dynamic performance. Fig. 14 illustrates the hydrogen capacity of nanoconfined, stoichiometric, magnesium hydride embedded hollow three-dimensional architecture of carbon during hydrogenation and dehydrogenation processes. The results show that the catalytic effect of a carbon structure plays a crucial role in enhancing the hydrogen storage performance of the carbon-based hydrides. The unique nanostructures of carbon show a promising effect as diffusion channels for hydrogen, resulting in dissociation of hydrogen molecules and enhancement in sorption kinetics. Gattia et al[34] found that Fe and its oxides are suitable catalysts for MgH_2 and they drastically speed up reaction kinetics. In the process of absorbing and releasing hydrogen, Fe and its oxides will rapidly transform into each other, thus reducing the activation energy. Besides, the doping of Fe and Co also improves the catalytic effect on hydrogen absorption of Mg composites as refer to Ref.[35].

2.2 Effect of nanocrystallization on the thermodynamic properties of hydrogen absorption and desorption of Mg

A distinctive feature of nanomaterials (such as nanoparticles, nanowires and thin films) is the high ratio between the total interface area and volume. The surface forms a special solid-vapor interface, and the thermodynamics of hydride formation will be changed when the free energy per unit area of metal state and hydride is different[36]. Both Wagemans[37] and Li et al[38] confirmed that reducing the size of Mg or MgH_2 nanoparticles can significantly reduce the dehydrogenation temperature based on Hartree-Fock theory and density functional theory (DFT). This conclusion is confirmed by experiments. Jeon et al[25] found that the hydrogen desorption temperature of Mg nanoparticles is dropped to 200 °C after decreasing its size to about 4.9 nm.

Fig.15 shows the curves of pressure vs hydrogen content of the $Mg_{2.9}Ni$ thin film measured at different temperatures[39]. The minimum desorption temperature of $Mg_{2.9}Ni$ is 497 K, which is far lower than that of the conventional value. This phenomenon is mainly due to the reduced energy barrier of new phase formation caused by the greatly increased interface energy of nanocrystalline Mg and Mg_2Ni. To stabilize the Mg/MgH_2 composite at the nano scale, one recently developed approach is to confine Mg/MgH_2 in a scaffold or matrix. Konarova et al[40] synthesized MgH_2 particles by wet impregnation within the pores of the mesoporous materials SBA15 and CMK3. The loading capacity of MgH_2 in CMK3 was designed as 20wt%, 40wt%, 60wt% and 80wt%. The results show that the peak desorption temperature drops with decreasing the loading capacity of MgH_2, the value is 358 °C at 90wt% loading and decreases to 253 °C at 20wt% loading.

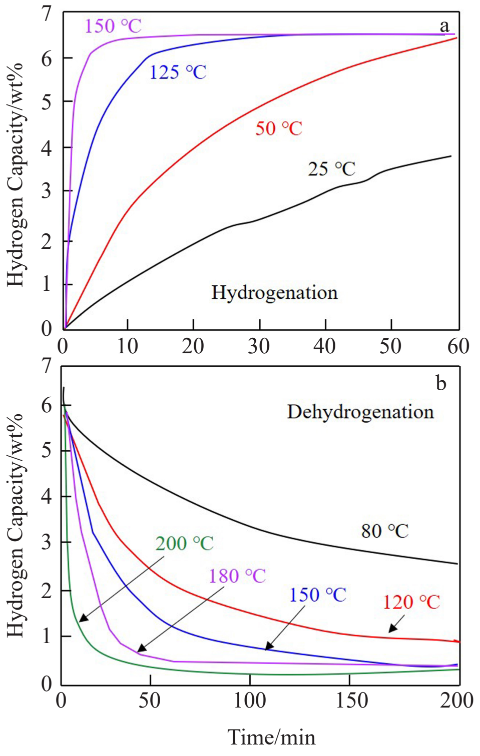

Fig.14 Hydrogen absorption (a) and desorption (b) curves of the nanoconfined, stoichiometric, magnesium hydride embedded hollow three-dimensional architecture of carbon at different temperatures[29]

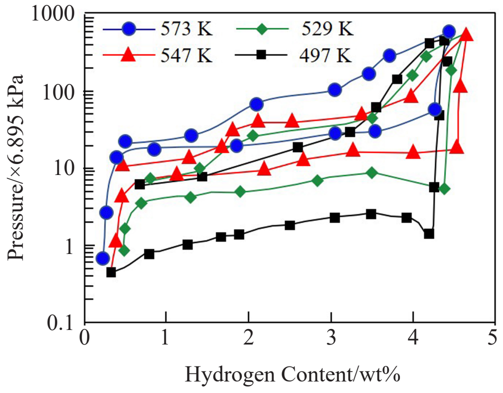

Fig.15 Curves of pressure vs hydrogen content of the Mg2.9Ni thin film at different temperatures: (a) 573 K, (b) 547 K, (c) 529 K, and (d) 497 K[39]

2.3 Effect of nanocrystallization on the kinetic properties of hydrogen absorption and desorption of Mg

Various defects in the alloy have been found to improve the hydrogen storage kinetics of Mg-based alloy. Dislocation, stacking fault, grain boundary, etc, favor hydrogenation and dehydrogenation kinetics without reducing storage capacity or increasing cost[8,41-44]. During the ball milling processing, Mg_2Ni can be protected by hydrogen, which may react with Mg_2Ni alloy[45,46]. The products of ball milling method thus have a good hydrogen absorption property. In addition, the hydrogen absorption and release temperature can also be reduced to 140 and 250 °C, respectively[47,48].

Zhang el al[49] prepared monodispersed Mg_2NiH_4 nanoparticles onto the graphene layer surface using the HCVD method. The products have a stable structure and an excellent dehydriding kinetic rate. The MgO layer divorces the nanoparticles to prevent accumulation from each other, and hinders the oxidation of Mg_2NiH_4. Finally, a low activation energy of hydrogen release action was accomplished. Tran el al[50] also found comparable consequences in various alloys with various defects and cracks inside during the hydrogenation/dehydrogenation cycles. Various defects such as vacancies and dislocations are found in front of the Mg/MgH_2 interface in hexagonal closed-packed structure systems including FeTi[51, 52]and $LaNi_5$[53]. The misfits introduced by the defects retain the lattice coherency elastic strain during phase transformation process and promote the activation of hydrogen storage materials[54]. Studies also found that grain boundaries serve as hydrogen diffusion pathways and promote the kinetics of the hydrogen storage alloys[55-60].

3 Summary and Prospect

Overall, the hydrogen absorption and desorption performance of Mg-bases alloys can be greatly improved by nano refinement technology. This makes nanostructured Mg a very promising hydrogen storage material. However, the improvement of hydrogen storage performance of nanostructured Mg still has some limitations. First, the improvement of thermodynamic performance is not obvious, and the temperature of hydrogen absorption and desorption is still high. Second, the dynamic performance will decline rapidly with the increase of hydrogen absorption and desorption times. The size of nanostructured Mg needs to be reduced to 10 nm or even less than 1 nm to accomplish a significant improvement in the thermodynamic properties. This puts forward a very high requirement for the preparation technology of nanostructured Mg. Although some scholars use doping to reduce the temperature of hydrogen absorption and desorption, the effect is still very restricted. At present, continuous refinement of nanostructured Mg is the main idea to improve the thermodynamic performance. There are still some limitations in the current processing technologies, and some new technologies need to be developed

During the service process, nanostructured Mg will grow and lose the small size effect, resulting the degradation of dynamic properties. This may be achieved by coating a layer of materials with isolation around nanoparticles or nanowires. However, there is few in-depth study in this filed, which can be one of the future research directions. Doping or surface modification can significantly improve the hydrogen absorption and desorption performance of nanostructured Mg, but it also shows a decline with the increase of hydrogen absorption and desorption time. This is mainly due to the fact that Mg atoms migrate to cover the doped catalyst nanoparticles after multiple hydrogen absorption and desorption, leading to the failure of the catalyst. How to keep the catalyst nanoparticles in contact with H_2 is the key in the future research of doping technology.

As mentioned above, metal hydride hydrogen storage is more secure when compared with gaseous high-pressure hydrogen storage and liquefied hydrogen storage. Hydride based solid-state hydrogen storage has the advantages of reversible cycle, relatively mature preparation technology and process, and is considered to be the most promising hydrogen storage method. Metal based hydrogen storage alloy materials are mainly divided into magnesium series, rare earth series and titanium series. Mg-based hydrogen storage material have become one of the most promising solid hydrogen storage materials due to its high hydrogen storage capacity, abundant raw materials, low price and high purity of hydrogen released[61-65]. Although there is still a certain distance from the practical application of nanostructured Mg, the preparation and modification of nanostructured Mg will be developed rapidly, considering the continuous attention to clean energy and the huge investment in the field of hydrogen energy in the world. It is no doubt that Mg-based alloys will play an important role in the utilization of hydrogen energy in the future.

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纳米结构镁的制备及其储氢性的研究进展

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摘　要：氢能的利用越来越受到人们的重视，而氢的储存和运输限制了其广泛的实际应用。镁基合金作为一种固体储氢材料，在储氢领域显示出巨大的潜力。但是，吸放氢温度高，释氢速率慢，阻碍了其工程应用。为了提高镁基合金的储氢能力，目前的研究主要集中在合金成分的优化和加工工艺的改进方面，而纳米细化是最有前途的方法之一。详细介绍了纳米镁的各种制备工艺，包括高能球磨、物理气相沉积、氢化化学气相沉积、液相化学合成和模板法，并分析了各种方法的优缺点。阐述了纳米结构和元素掺杂对镁基合金储氢性能的影响。本研究为储氢领域的材料开发和制备工艺的改进提供参考。

关键词：氢能；镁基合金；纳米细化；储氢性能；释氢性能

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