Nucleation and recombination dependent desorption performance of Mg-based hydrides

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Abstract. High desorption temperature and sluggish desorption kinetics hinder the large-scale application of Mg-based hydrogen storage materials. Fundamental understanding of the dehydrogenation process and underlying mechanism is crucial for further modifying the desorption performance. Aiming at elucidating the dehydrogenation process of Mg-based hydrides, partially desorbed pure MgH₂ and MgH₂-Mg₂NiH₄-CeH₂.⁷³ composite have been prepared to investigate the effects of metal phase nucleation on overall desorption performance. It is found that metal Mg is formed on the surface of partially desorbed MgH₂ and MgH₂-Mg₂NiH₄-CeH₂.⁷³. Correspondingly, the desorption temperature of partially desorbed samples is significantly decreased, indicating an important role nucleation plays in desorption process. With minor Ni addition, the desorption temperature and kinetics of MgH₂-Mg₂NiH₄-CeH₂.⁷³ are significantly improved. Promoting hydrogen recombination is another essential aspect to modify the desorption properties of Mg hydrides.

1. Introduction

With the increasing concern on energy shortage and environmental pollution, substitutes for the present energy technologies relying on fossil fuels are highly desired [1]. Hydrogen is an outstanding renewable energy carrier considering its abundant sources, high energy density and water as the only combustion product. Three critical technologies need to be solved for the effective use of hydrogen: inexpensive and efficient hydrogen production technology, safe and reliable hydrogen storage technology, economic and reasonable hydrogen utilization technology. Hydrogen storage technology is still immature, limiting its extensive application [2]. Exploring a safe and efficient storage method is the key to hydrogen energy.

Although some new kinds of materials such as borohydrides, amides and alanates have been intensively studied, Mg-based materials are still considered to be the most promising materials because of the low cost, high capacity and environmental friendliness. However, the high desorption temperature and slow desorption kinetics hinder its practical applications. The strategies commonly adopted to improve the desorption performance include nanostructuring, alloying and doping catalytic components [3-5]. The grain size or particle size of Mg can be even decreased to few nanometers by ball milling, melt spinning, physical deposition, wet chemical routes and electrochemical approaches [6, 7]. The catalysts used to modify the surface characteristics include metals, oxides, hydrides, carbon materials et al [8, 9]. Significant progress has been made by the newly developed ball-milling with
aerosol spraying, which shows much higher mechanical alloying efficiency in preparing hydrogen storage materials [10, 11].

Although all kinds of techniques have been tried to improve the performance of Mg-based materials, the reasons for such slow kinetics are still obscure. It is usually considered that the desorption process consists of the nucleation and growth of metal phase, the diffusion and recombination of hydrogen [12]. Advanced preparing methods and fundamental knowledge of desorption mechanisms are crucial to enhance the dehydrogenation properties of Mg-based alloys. Understanding the determining factors and rate-limiting steps of desorption contributes to the development of new ideas and methods for preparing Mg-based alloys.

This work aims to elucidate the dehydrogenation factors of Mg-based hydrogen storage materials. Special attention is paid to the Mg nucleation and hydrogen recombination during dehydrogenation process. Partially dehydrogenated pure MgH2 and MgH2-Mg2Ni-CeH2.73 composite and Ni catalyzed MgH2-Mg2Ni-CeH2.73 composite are carefully prepared. The microstructure characteristics and dehydrogenation performance of prepared samples are also investigated.

2. Experimental

MgH2 powders purchased from Alfa Aesar without any further processing were used as the starting materials (mean size: ~44 μm, 98% purity). The Mg-Ni-Ce alloy with nominal composition of Mg-5Ni-5Ce (wt.%) was melted in graphite crucible. Detailed preparation process has been described in Ref [13]. The as-melt alloy was then ball milled for 2 h and activated through three cycles of hydrogenation and dehydrogenation at 350 °C. After activation, MgH2-Mg2NiH4-CeH2.73 composite hydrides were obtained [13]. To investigate the influences of nucleation of Mg and recombination of hydrogen during dehydrogenation process on the overall dehydrogenation properties, partially dehydrogenated and Ni-catalyzed samples were prepared.

To achieve partially dehydrogenated powders of MgH2 and MgH2-Mg2NiH4-CeH2.73, differential scanning calorimetry measurement was performed on a DSC/DTA-TG apparatus (STA449F1). Firstly, as-received MgH2 and MgH2-Mg2NiH4-CeH2.73 composite were heated to 500 °C to obtain the DSC curves of complete desorption. Referring to the obtained DSC curves of MgH2 and MgH2-Mg2NiH4-CeH2.73, 429 °C and 330 °C were then selected as the final heating temperatures in the following DSC measurements of as-received MgH2 and MgH2-Mg2NiH4-CeH2.73 to achieve partially desorbed samples, respectively. The partially dehydrogenated MgH2 and MgH2-Mg2NiH4-CeH2.73 were quenched to 50 °C immediately after reaching 429 °C and 330 °C to preserve the microstructures as much as possible. Finally, the partially dehydrogenated samples were heated to 500 °C to measure the desorption performance.

It has been proved that Ni significantly promotes the recombination of hydrogen atoms and preserves little influence on other processes [14]. Therefore, the as-activated MgH2-Mg2NiH4-CeH2.73 samples were ball milled with 10wt.%Ni for 1 h to investigate the effect of hydrogen atom recombination. Simultaneously, the as-received MgH2-Mg2NiH4-CeH2.73 composite was also milled for 1 h with the same ball to powder weight ratio (20:1).

The microstructure characteristics of the as-received and partially desorbed pure MgH2, as-activated and partially desorbed MgH2-Mg2NiH4-CeH2.73 and Ni catalyzed MgH2-Mg2NiH4-CeH2.73 composite was characterized by scanning electron microscopy (SEM/BSE). The metal powders were scattered on the conducting resin without any coating process. The dehydrogenation kinetics of prepared samples was measured by DSC/DTA-TG up to 500 °C under 30 ml/min flowing argon gas. The heating rate was 10 °C/min for each DSC measurement.

3. Results and discussions

3.1. Partial desorption of MgH2

The DSC curves of as-received MgH2 powders with final heating temperatures of 500 °C and 429 °C are shown in Figure 1(a). The corresponding TGA curves are shown in Figure 1(b). For as-received
MgH$_2$ with a final heating temperature of 500 °C, the onset desorption temperature and peak temperature are ~420 °C and ~436 °C, respectively. Consequently, 429 °C is selected as the final heating temperature in subsequent DSC measurement to achieve partially dehydrogenated MgH$_2$ powders. For partially dehydrogenated MgH$_2$ heated to 500 °C, the onset desorption temperature is ~378 °C, much lower than that of as-received MgH$_2$. It can be drawn from the results that Mg nucleation during dehydrogenation of MgH$_2$ affects the desorption temperature significantly. In other words, generated Mg during partial desorption can effectively reduce the desorption temperature when partially dehydrogenated MgH$_2$ desorbing again.

Figure 1. (a) DSC and (b) TGA curves of as-received and partially desorbed MgH$_2$ at final heating temperatures of 500 °C and 429 °C.

During partial dehydrogenation measurement of MgH$_2$, the partially dehydrogenated MgH$_2$ sample was quenched to 50 °C immediately after reaching 429 °C. SEM/BSE images of as-received and partially desorbed MgH$_2$ are illustrated in Figure 2. Newly generated Mg and undecomposed MgH$_2$ can be obviously distinguished from the SEM/BSE images based on the average atomic number (Mg: 12, MgH$_2$: 4.67) [15]. Metal Mg phase is much brighter than MgH$_2$ phase in backscattered SEM image. Primary-formed Mg can reduce the nucleation barrier in subsequent dehydrogenation process.

Figure 2. SEM/BSE images of (a) as-received and (b) partially dehydrogenated MgH$_2$ powders.

3.2. Partially dehydrogenated and Ni catalyzed MgH$_2$-$\text{Mg}_2\text{NiH}_4$-$\text{CeH}_2.73$

Similarly, partial dehydrogenation measurement of MgH$_2$-$\text{Mg}_2\text{NiH}_4$-$\text{CeH}_2.73$ composite by DSC has also been performed. Figure 3 illustrates the corresponding DSC and TGA curves. For complete dehydrogenation of as-activated MgH$_2$-$\text{Mg}_2\text{NiH}_4$-$\text{CeH}_2.73$, the onset desorption temperature and peak temperature are ~315 °C and ~336 °C, respectively. Therefore, 330 °C is selected as the final heating
temperature in subsequent DSC measurement to obtain partially dehydrogenated MgH$_2$-Mg$_2$NiH$_4$-CeH$_{2.73}$ sample.

Figure 3. (a) DSC and (b) TGA curves of as-activated MgH$_2$-Mg$_2$NiH$_4$-CeH$_{2.73}$ powders at final heating temperatures of 500 °C and 330 °C, the DSC and TGA curves of partially dehydrogenated MgH$_2$-Mg$_2$NiH$_4$-CeH$_{2.73}$ are also given in (a) and (b), respectively.

Figure 4 displays the SEM/BSE images of as-activated and partially dehydrogenated MgH$_2$-Mg$_2$NiH$_4$-CeH$_{2.73}$ powders. Newly generated Mg and undecomposed MgH$_2$ are also clearly observed. As to desorption of partially dehydrogenated MgH$_2$-Mg$_2$NiH$_4$-CeH$_{2.73}$ shown in Figure 3, the onset desorption temperature is ~265 °C, much lower than that of as-activated powder.

Figure 4. SEM/BSE images of (a) as-activated and (b) partially dehydrogenated MgH$_2$-Mg$_2$NiH$_4$-CeH$_{2.73}$ powders.

Hydrogen atoms are difficult to recombine to hydrogen molecules on the surface of pure Mg due to the electronic structure characteristics. However, some transition metals such as Ni and Pd are reported to effectively accelerate the recombination of hydrogen atoms on their surface, which is ascribed to the interactions between d-orbitals and hydrogen antibonding orbital [16]. Ni has been proved to be the best choice among transition metals to promote hydrogen combination without affecting other processes such as matrix agglomeration, hydrogen atom diffusion and hydrogen molecule desorption [17]. It has been reported that Ni can attract both H and Mg atoms, increasing the local coordination and creating voids on longer distances by density functional theory [18]. In this work, 10wt.% Ni is ball milled with as-received MgH$_2$-Mg$_2$NiH$_4$-CeH$_{2.73}$ composite for 1 h in Ar to investigate the effect of hydrogen recombination on overall dehydrogenation process. The as-activated MgH$_2$-Mg$_2$NiH$_4$-CeH$_{2.73}$ composite is also ball milled for 1 h in Ar with the same ball to powder ratio for comparison. Figure 5(a) shows the SEM/BSE image of Ni catalyzed MgH$_2$-Mg$_2$NiH$_4$-CeH$_{2.73}$ powders, displaying the uniform distribution of Ni. The desorption DSC curves of as-milled and Ni
catalyzed MgH$_2$-Mg$_3$NiH$_4$-CeH$_{2.73}$ samples are illustrated in Figure 5(b). The onset desorption temperature for as-milled MgH$_2$-Mg$_3$NiH$_4$-CeH$_{2.73}$ sample is ~300 °C, while it is ~200 °C for Ni catalyzed MgH$_2$-Mg$_3$NiH$_4$-CeH$_{2.73}$. With Ni addition, the desorption temperature and kinetics improve significantly, indicating an important role of hydrogen recombination. Promoting the recombination of hydrogen atoms is another key factor to modify the dehydrogenation performance of Mg-based materials.

Figure 5. (a) SEM/BSE image of Ni catalyzed MgH$_2$-Mg$_3$NiH$_4$-CeH$_{2.73}$ and (b) DSC curves of as-milled and Ni catalyzed MgH$_2$-Mg$_3$NiH$_4$-CeH$_{2.73}$.

Coarse Mg-based materials are not suitable for hydrogen storage purpose. Up to the present, numerous innovative approaches are available to synthesize Mg-based nanomaterials [19, 20]. Both the grain and particle sizes of Mg and Mg-based materials can even reach a few nanometers [21]. Finer grain or particle implies shorter diffusion distance of hydrogen. Considering the reported diffusion rate of hydrogen in pure Mg (4×10$^{-13}$ m$^2$/s [22]) and MgH$_2$ (1.5×10$^{-16}$ m$^2$/s [23]), hydrogen atoms are effortless to diffuse through MgH$_2$ or Mg particles with diameters of several tens of nanometers. During dehydrogenation, the diffusion energy needed for hydrogen atoms is probably unimportant in Mg and Mg-based nanoparticles.

Therefore, special attention should be paid to decrease the nucleation barrier and promote the hydrogen recombination. Strategies simultaneously and effectively tuning Mg nucleation and hydrogen recombination should be explored in future work. If artificially added Mg or other effective additives can be mixed with MgH$_2$ at the atomic scale, the desorption temperature will decrease significantly. Nucleation energy, nucleation sites and their stabilization, hydrogen recombination barrier, sites of hydrogen atom enrichment, selection and distribution of additives should be taken into consideration. Although Ni is an effective element to accelerate hydrogen recombination, it reacts with Mg to form Mg$_2$Ni after few absorption and desorption cycles at temperatures suitable for dehydrogenation [24].

Strategies such as nanostructuring, synthesizing metastable phases, doping catalytic additives and preparing nanocomposites have made breakthroughs to modify the thermodynamics and kinetics of MgH$_2$ dehydrogenation [1, 25]. However, as long as the desorption temperature is not decreased obviously, the excellent structural characteristics are easy to disappear. Increasing vacancies or octahedral/tetrahedral sites by amorphization, which can accommodate hydrogen atoms, can modify the capacity and decrease the desorption temperature [26]. Discovering advanced approaches to retain the structural stability of nanostructuring, such as introducing a second phase, carbon nanoribbons and core-shell structure are necessary [27].

4. Conclusions
The effects of Mg nucleation and hydrogen recombination on overall desorption performance of pure MgH$_2$ and MgH$_2$-Mg$_3$NiH$_4$-CeH$_{2.73}$ composite have been investigated in this work. For partially dehydrogenated MgH$_2$, the onset desorption temperature decreases from 420 °C to ~378 °C. The onset
desorption temperature is ~265 °C for partially dehydrogenated MgH$_2$-Mg$_2$NiH$_4$-CeH$_{2.73}$, much lower than that of as-activated powder. After ball milling with 10wt.%Ni, the desorption temperature of MgH$_2$-Mg$_2$NiH$_4$-CeH$_{2.73}$ can be reduced to ~200 °C, indicating recombination of hydrogen atoms also affects the desorption process significantly. Strategies simultaneously tuning Mg nucleation and hydrogen recombination effectively should be preferentially considered in future work.

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References
[1] Ouyang L, Liu F, Wang H, Liu J, Yang X, Sun L 2020 Journal of Alloys and Compounds 832 154865
[2] Jia Y, Sun C, Shen S, Zou J, Mao S, Yao X 2015 Renewable and Sustainable Energy Reviews 44 289-303
[3] Zhang Y, Wei X, Yuan Z, Hou Z, Qi Y, Guo S 2020 Journal of Physics and Chemistry of Solids 138 109252
[4] Song W, Dong H, Zhang G, Liu J, Yang G, Liu Y 2020 Journal of Alloys and Compounds 820 153187
[5] Leiva DR, Jorge JAM, Ishikawa TT, Botta WJ 2019 Materials Transactions 60 1561-1570
[6] Zhang J, Li Z, Wu Y, Guo X, Ye J, Yuan B 2019 RSC Advances 9 408-428
[7] Huot J, Tousignant M 2019 Materials Transactions 60 1571-1576
[8] Song MY, Choi E, Kwak YJ 2020 Materials Research Bulletin 130 110938
[9] Webb CJ 2015 Journal of Physics and Chemistry of Solids 84 96-106
[10] Ding Z, Li H, Shaw L 2020 Chemical Engineering Journal 385 123856
[11] Ding Z, Shaw L 2019 ACS Sustainable Chemistry & Engineering 7 15064-15072
[12] Aguey-Zinsou KF, Ares-Fernández JR 2010 Energy & Environmental Science 3 526-543
[13] Xie L, Li J, Zhang T, Song L, Kou H 2017 Journal of Power Sources 338 91-102
[14] Jensen T, Andreasen A, Vegge T, Andreasen J, Stahl K, Pedersen A 2006 International Journal of Hydrogen Energy 31 2052-2062
[15] Antisari MV, Montone A, Aurora A, Mancini MR, Gattia DM, Pilloni L 2009 Intermetallics 17 596-602
[16] Frey GD, Lavallo V, Donnadieu B, Schoeller WW, Bertrand G 2007 Science 316 439-441
[17] Pozzo M, Alfé D 2009 International Journal of Hydrogen Energy 34 1922-1930
[18] Giusepponi S, Celino M 2015 International Journal of Hydrogen Energy 40 9326-9634
[19] Rango P, Fruchart D, Aptukov V, Skryabina N 2020 International Journal of Hydrogen Energy 45 7912-7916
[20] Gajdics M, Spassov T, Kis VK, Schafler E, Révész Á 2020 International Journal of Hydrogen Energy 45 7917-7928
[21] Aguey-Zinsou KF, Ares-Fernández JR 2008 Chemistry of Materials 20 376-378
[22] Töppler J, Buchner H, Säufler H, Knorr K, Prandl W 1982 Journal of the Less Common Metals 88 397-404
[23] Nishimura C, Komaki M, Amano M 1999 Journal of Alloys and Compounds 293-295 329-333
[24] House SD, Vajo JJ, Ren C, Rockett AA, Robertson IM 2015 Acta Materialia 86 55-68
[25] Li B, Li J, Zhao H, Yu X, Shao H 2019 International Journal of Hydrogen Energy 44 6007-6018
[26] Patelli N, Migliori A, Morandi V, Pasquini L 2020 Nano Energy 72 104654
[27] Cho ES, Ruminski AM, Liu YS, Shea PT, Kang SY, Zaia EW 2017 Advanced Functional Materials 27 1704316