The Pd catalyst effect on low temperature hydrogen desorption from hydrided ultrathin Mg nanoblades

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Abstract

We present hydrogenation/de-hydrogenation properties of ultrathin Mg nanoblades coated with Pd as a catalyst. The hydrided Pd/Mg/Pd and Pd/Mg nanoblades were highly curved as observed by \textit{ex situ} scanning electron microscopy. An \textit{in situ} thermal desorption spectroscopy (TDS) study showed that the hydrided Pd/Mg/Pd nanostructure has a low hydrogen desorption temperature, at \(\sim 365 \text{ K}\). Through a combinational microstructure and TDS analysis of hydrided Pd/Mg/Pd nanoblades as well as hydrided Pd/Mg/Pd nanoblades covered with an additional ultrathin Mg layer, we found that the effect of Pd catalyst on reducing the hydrogen desorption temperature is significantly stronger than the conventionally proposed mechanisms due to grain size and strain.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Magnesium is a very attractive material for hydrogen storage because it is abundant and has a low density (1.738 g cm\(^{-3}\)). Theoretically, magnesium hydride (MgH\(_2\)) contains 7.6 wt\% of hydrogen, which is above 6 wt\% required by DOE hydrogen plans. However, due to the ionic bond nature between Mg and H atoms, MgH\(_2\) is thermodynamically stable \cite{1}. Additionally, the hydrogenation/de-hydrogenation of Mg is also kinetically hindered by a number of barriers. For example, the hydrogen molecules do not readily dissociate on the Mg surface with an energy barrier of \(\sim 1.1 \text{ eV}\) \cite{2, 3}. Hydrogen atoms also have an extremely slow diffusion in magnesium hydride. All these factors make the hydrogen kinetics of magnesium sluggish unless the material is heated to \(\sim 573–673 \text{ K}\).

Various strategies have been explored to enhance the hydrogen kinetics of magnesium hydride. One method is to fabricate the Mg particles to nanometers scale size. For example, using mechanical ball milling, Zaluska \textit{et al} \cite{4, 5} have created nanocrystalline Mg and Mg\(_2\)Ni, which showed one order of magnitude faster kinetics of hydrogen absorption and desorption than their corresponding bulk materials. However, the problems, such as contamination and oxidation during the mechanical ball milling, remain to be solved \cite{6}. In addition, the bulk Mg material can hardly be ground into particles with a diameter less than 100 nm. Very recently, Mg nanowires with a diameter down to \(\sim 30 \text{ nm}\) have been fabricated by a vapor-transport approach \cite{7}. The addition of a catalyst is another method used extensively to overcome the inherent limitations of pure Mg \cite{8–10}. Since catalysts basically work at the surface of materials, their functionality is very sensitive to contamination and oxidation on surfaces. Pd Coated Mg thin films have been demonstrated to have the most impressive hydrogen kinetics with a low desorption temperature peak of \(\sim 373 \text{ K}\) \cite{11–14}. The enhanced catalyst functionality is essentially attributed to the film preparation in a high vacuum condition, which gives minimum contamination and oxidation on surfaces. However, the continuous film structure limits the catalytic effect to the top \(\sim 200 \text{ nm}\) of the film leaving the rest of the Mg film without this catalytic advantage \cite{13}.

In this paper, we reported hydrogenation/de-hydrogenation properties of ultrathin Mg nanoblades (\(\sim 15 \text{ to } \sim 30 \text{ nm}\) thick) coated with Pd as a catalyst. This unique composite nanostruc-
tut has shown a low hydrogen desorption temperature peak at $\sim$365 K. Through the analyses of hydrided nanoblades by ex situ scanning electron microscopy (SEM), transmission electron microscopy (TEM) and in situ thermal desorption spectroscopy (TDS), we have revealed that the Pd catalyst plays a more important role in reducing the hydrogen desorption temperature than other possible factors, such as grain size and strain [11, 14].

2. Experiments

The Pd coated nanoblades were prepared in an ultrahigh vacuum (UHV) chamber equipped with Mg and Pd thermal evaporation sources. We first grew Mg nanoblades on the Si substrate by oblique angle deposition (OAD). During deposition the Mg vapor flux was incident on the substrate at 75° with respect to the substrate normal [15]. The deposited nanoblades are nearly vertically standing with an angle slightly tilted away from the flux [16]. In order to coat Pd over the entire length Mg nanoblades, the substrate was first rotated about the substrate normal, so that the vertical Mg nanoblades were approximately aligned with the Pd flux direction. Then during the Pd evaporation we either coated one side of the nanoblades with the substrate stationary or swung the substrate polarly in an angular range of $\sim$15° to achieve the coatings on both sides of the nanoblades. During the growth of Mg and Pd the pressure increased from the base pressure of $\sim$3.0 $\times$ 10$^{-9}$ Torr to $\sim$2.0 to 3.0 $\times$ 10$^{-8}$ Torr. The evaporation rate of Mg was maintained between $\sim$9.0 and $\sim$12.0 nm min$^{-1}$ as indicated by a quartz crystal monitor (QCM). The Pd growth rate was $\sim$0.12 nm min$^{-1}$ and a total of $\sim$4 to 6.5 nm Pd was deposited based on the reading from the QCM. After the Pd coating, the Mg nanoblades were transported in situ from the deposition chamber to the reaction chamber connected by an in-line valve. The composite nanoblades were hydrogenated at a pressure of 1 bar with substrate held at $\sim$333 K for $\sim$15 h.

The TDS was used to investigate the de-hydrogenation kinetics under a base pressure $\sim$1.5 $\times$ 10$^{-8}$ Torr after venting and degassing the reaction chamber. The temperature rising rate for TDS was $\sim$3 K min$^{-1}$. A residue gas analyzer (RGA) was used to measure the amount of desorbed hydrogen gas by monitoring the H$_2$ partial pressure as a function of time (or temperature through heating rate).

3. Results and data analyses

3.1. SEM analyses

Figure 1(a) shows the ex situ SEM cross-section image of the as deposited Mg nanoblade film with one side of nanoblade coated with Pd (named Pd/Mg nanoblades). From the image, we can see that the as deposited nanoblades were slightly curved. After the hydrogenation in the reaction chamber, the Pd/Mg nanoblades became highly curved and bent obviously towards the incident vapor fluxes, as shown in figure 1(b). It is known that there is a $\sim$30% volume expansion during the transformation from Mg to MgH$_2$. This volume change can yield a considerable stress [14, 17, 18] and cause the deformation of nanostructures. Since only one side of each nanoblade was coated with Pd, we may intuitively think the Pd coated side was more hydrided and extended more. However, if this picture was correct, the nanoblades should bend to the side without Pd coating, specifically these should bend away from the fluxes, which is opposite to our experimental observations. It was also reported [13] that with a Pd coating the Mg thin films can be hydrided up to a depth of $\sim$200 nm beneath the surface. Therefore, the entire thickness of nanoblades ($\sim$15 to $\sim$30 nm) around the Pd coating very likely has been fully hydrided. Another possible mechanism for the curvature formation of nanoblades is the decomposition of the hydrided nanoblades. From previous studies [11, 12], it was shown that the MgD$_2$ film with Pd coating partially was decomposed into Mg in air. The MgD$_2$ has an identical chemical property as MgH$_2$. In this case the Mg hydride near the Pd coating side will be decomposed, which results in the bending of nanoblades towards the flux. This picture is more consistent with our experimental observations. The further decomposition of MgH$_2$ may be prevented by the Mg oxide layer formed between Pd and MgH$_2$ in air [19]. Assuming the formation of a bilayer with an equal thickness of Mg and MgH$_2$, then the strain produced due to the decomposition of MgH$_2$ can be calculated from $2t/(3R)$, where $R$ is the radius of the curvature [20]. By fitting the curliest nanoblade, as shown in figure 1(c) we can obtain the radius of the curvature, $R \sim 200$ nm. Then the calculated strain required to produce this curvature is equal to $2t/(3R) = 6.6\%$, by using an average $t$ of $\sim$20 nm. This value of required strain is smaller than the value that can be theoretically produced by MgH$_2$ and Mg bilayer, which is $\sim$8.37%. This theoretical strain is calculated from $(1 - (1/1.3)^{1/3}) = 8.37\%$ assuming a $\sim$30% isotropic volume change during the decomposition.

In addition to the circularly curved nanoblades, many helical structures also exist, shown in the SEM top view image of figure 1(c). This helical structure is due to the non-uniform coating of Pd on the particular nanoblades. For example, if the non-uniform coating produces a strain along the diagonal direction instead of the edge of the nanoblades, then the nanoblades will curve into a helical shape to release the generated strain [20].

Figure 1(d) shows an ex situ SEM image of hydrided Mg nanoblades with Pd coating on both sides (Pd/Mg/Pd nanoblades). From the image we can see that the nanoblades are less curved and there is no obviously preferred bending direction any more. Since the Pd coating along the nanoblade length is not uniform, then at a particular height of a nanoblade the coating of Pd on both sides of a nanoblade can be very different. However, this difference in coating varies along the nanoblade length, resulting in the disappearance of a preferred bending direction. In our later analysis, we will concentrate on the nanoblades with Pd coating on both sides, which is more resistive to the oxidation in air.

3.2. TEM images

The microstructure of the air exposed hydrided nanoblades with Pd coating on both sides was further examined ex situ
using TEM. Figure 2(a) shows the bright field image of hydrided nanoblades. Using the electron energy loss spectroscopy (EELS) mapping mode in TEM, we investigated the Pd element distribution in the nanoblades. The inset of figure 2(a) is a typical Pd distribution map obtained by using the Pd M_{4,5} peak (335 eV). The bright areas in the map contain a higher Pd concentration than the dark areas. The map indicates a non-continuous coating of Pd on the nanoblades. Since the thickness of the Pd coating on the nanoblades was on the order of a few nanometers, the growth may still be in the island nucleation stage. Moreover, the Pd flux was obliquely incident on the side faces of the nanoblades thereby enhancing the island formation due to shadowing effect [21–23]. We estimated the average Pd coverage from the multiple Pd EELS images of the nanoblades. The analysis software used for calculating the coverage is UTHSCSA ImageTool [24]. In the calculation from one Pd EELS image we considered that the dark area of the image has no Pd coverage and the bright and white area with EELS intensity greater than zero has Pd coverage. The estimated coverage was calculated by taking the ratio between the total area of all the bright and white regions and the total area of the image. The coverage of Pd coating varied along the length of the nanoblade, which yields a large standard error of 23% in the estimated value of 60 ± 23% from multiple Pd EELS images.

This Pd coating is very important to the hydrogenation process as the hydrogen molecules were dissociated by Pd to...
provide atomic hydrogen [19, 25]. As we will show later, Pd also plays a critical role in assisting the hydrogen desorption in the de-hydrogenation process.

Figures 2(b) and (c) are selected area electron diffraction (SAED) patterns taken from the circled regions on the hydrided nanoblade. The patterns consist of diffraction rings and spots. By measuring the corresponding reciprocal lattice distances in the diffraction pattern, we identified the crystalline phases and indexed the diffraction pattern as shown in figures 2(b) and (c). The obvious diffraction rings of MgH\(_2\)(110) and MgH\(_2\)(200) indicate a significant hydride in the air exposed nanoblade. We can also see the Mg phase in this air exposed sample as represented by diffraction spots. However these diffraction spots scattered and did not form a single crystalline pattern as in the pure Mg nanoblades [15]. This shows that the remaining Mg crystallites have been reoriented [15]. Figure 2(d) shows the high resolution transmission electron microscopy (HRTEM) image taken from the region near the edge of a nanoblade. The lattice fringes in the image mainly correspond to two interplanar distances from the measurement. One is 3.29±0.07 Å, which can only match with the interplanar distance of (110) planes of MgH\(_2\) at 3.19 Å. Some of these grains are outlined by white dashed curves. The size of the MgH\(_2\)(110) grains is ∼(5.3 ± 2.0) nm. The other one has an interplanar distance of 2.29 ± 0.06 Å, which is close to the interplanar distances of MgH\(_2\)(200) and Pd(111) which are 2.26 Å and 2.24 Å, respectively. These grains are outlined by white solid curves. In addition, we can see from figure 2(d) that a thin oxide layer ∼2 to ∼5 nm thick in the boundary region of the nanoblades exists. This thin oxide layer has a nearly amorphous structure, which is consistent with the very weak oxide diffraction rings in figures 2(b) and (c).

### 3.3. TDS measurement

The de-hydrogenation property of hydrided Pd/Mg/Pd nanocomposite structure was in situ characterized by TDS. Figure 3 shows the TDS spectrum of hydrided nanoblades. Two well separated hydrogen desorption peaks were observed in the spectrum. This suggests the existence of two different kinetic processes of hydrogen desorption. The major desorption peak occurs at ∼365 K while the other peak lies at a significantly higher temperature of ∼513 K. Repeated experiments on samples prepared under similar conditions showed that these two peaks can vary from ∼365 to 393 K and ∼503 to 560 K, respectively. Researchers have found the low temperature desorption peaks at the Pd/Mg thin film structure, which ranges from ∼388 to 483 K [11, 13]. However, the mechanism causing this desorption peak is still being debated. Different factors, such as Pd catalyst [9], crystal size and strain have been proposed [11, 13]. For a nanostructure, the strain can be mostly released through the free surfaces. Schimmel et al also demonstrated that the strain may not be the major factor for the enhanced hydrogen adsorption and desorption kinetics [26]. Another factor like grain size can significantly lower hydrogen desorption temperature only when the size of the MgH\(_2\) clusters is less than 1 nm [27]. Such a size is much smaller than our experimentally observed MgH\(_2\) grain size of ∼(5.3 ± 2.0) nm.

![Figure 3. In situ TDS spectra of hydrided Pd/Mg/Pd nanoblades (blue curve) and Mg coated hydrided Pd/Mg/Pd nanoblades (red curve).](image)

### 4. Discussion

Previous studies have illustrated the critical role of Pd catalyst in enhancing the hydrogenation kinetics of Mg. However, the effect of Pd on the de-hydrogenation process has been less studied [9]. To test this effect, we coated another thin layer of Mg on the hydrided Pd/Mg/Pd nanoblades. Our way of coating this Mg layer is basically similar to that of Pd coating, except with a larger substrate swing angular range (∼25°) and a much thicker Mg layer of ∼25 nm, in contrast with ∼6.5 nm thick Pd coating. The catalyst effect of Pd on the de-hydrogenation process is expected to be significantly reduced due to this additional Mg coverage. In the mean time, the grain size of MgH\(_2\) and strain remain unchanged in these Mg covered Pd/Mg/Pd nanoblades. From the TDS spectrum of the Mg coated hydrided Pd/Mg/Pd nanoblades shown in figure 3, we can clearly see that the first hydrogen desorption peak has been shifted to a significantly higher temperature of ∼503 K. This increased desorption temperature should be due to the loss of Pd catalyst effect. Although the detailed atomic process of catalysis is not clear, we believe that Pd may help the recombination process of H atoms into hydrogen molecules on the surface [3, 11]. Through the simulation prediction [3], Vegge has shown that the recombination barrier for a hydrogen molecule is the limiting factor for hydrogen desorption from pure Mg surface. The coated Mg may require H atoms to diffuse through an extra layer of Mg with a thickness up to ∼12.5 nm (half of ∼25 nm). However, this diffusion through a distance of tens of nanometer will take less than a microsecond [11]. Therefore, it is not an impeding factor to the hydrogen desorption process. We also observed another peak at ∼560 K, which is close to the desorption peak of pure MgH\(_2\) at ∼573 K [1]. This indicates that the Pd layer has almost fully lost its catalyst effect at this temperature.

The diminishing of Pd catalyst effect may also account for the higher temperature desorption peak observed from the hydrided Pd/Mg/Pd nanoblades. In the low temperature
desorption peak of $\sim 365$ K, the Pd can serve as a catalyst. However, after certain H desorption, the pure Mg will be produced around Pd. From the Pd mapping, we know that the Pd coating is not continuous, the deposited pure Mg will migrate and cover Pd clusters. This migration has been widely found [19, 28, 29]. Krozer et al. [19] has shown that at a temperature of $\sim 353$ K, Mg can migrate through 23 nm thick Pd coating and cover the top of Pd surface. Pd and Mg can also form alloys in the interface region at a temperature as low as 323 K [30, 31]. Once the Pd surface was fully modified to Pd coating and cover the top of Pd surface. Pd and Mg can migrate and cover Pd clusters. This migration has been widely found [19, 28, 29], Krozer [28] has shown that at a temperature of $\sim 353$ K, Mg can migrate through 23 nm thick Pd coating and cover the top of Pd surface. Pd and Mg can also form alloys in the interface region at a temperature as low as 323 K [30, 31]. Once the Pd surface was fully modified to Pd coating and cover the top of Pd surface. Pd and Mg can migrate and cover Pd clusters. This migration has been widely found [19, 28, 29], Krozer [28] has shown that at a temperature of $\sim 353$ K, Mg can migrate through 23 nm thick Pd coating and cover the top of Pd surface. Pd and Mg can also form alloys in the interface region at a temperature as low as 323 K [30, 31]. Once the Pd surface was fully modified to Pd coating and cover the top of Pd surface. Pd and Mg can migrate and cover Pd clusters. This migration has been widely found [19, 28, 29], Krozer [28] has shown that at a temperature of $\sim 353$ K, Mg can migrate through 23 nm thick Pd coating and cover the top of Pd surface. Pd and Mg can also form alloys in the interface region at a temperature as low as 323 K [30, 31]. Once the Pd surface was fully modified to Pd coating and cover the top of Pd surface. Pd and Mg can migrate and cover Pd clusters. This migration has been widely found [19, 28, 29], Krozer [28] has shown that at a temperature of $\sim 353$ K, Mg can migrate through 23 nm thick Pd coating and cover the top of Pd surface. Pd and Mg can also form alloys in the interface region at a temperature as low as 323 K [30, 31]. Once the Pd surface was fully modified to

## 5. Conclusion

In summary, we have observed the air exposed hydrided Pd/Mg/Pd and Pd/Mg nanoblades were highly curved. Through the analyses of hydrided Pd/Mg/Pd nanoblades and Mg covered hydrided Pd/Mg/Pd nanoblades by ex situ SEM, TEM and in situ TDS, we have revealed the importance of Pd catalyst on the hydrogen desorption process at low temperature. The understanding of the effect of Pd catalyst on the hydrogen desorption process at low temperature could be due to the oxide layer formed between Pd and Mg during the air exposure [32].

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