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Shape-Controlled Growth of MgH$_2$/Mg Nano/Microstructures Via Hydriding Chemical Vapor Deposition

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ABSTRACT

In this paper, we report the shape-controlled growth of MgH$_2$/Mg nano/microstructures via hydriding chemical vapor deposition (HCVD), wherein magnesium vapor was deposited on a substrate at different temperatures ranging from 225 °C to 600 °C and H$_2$ pressures ranging from 1 to 4 MPa. The products obtained after heating for 7, 13, and 20 h were identified by XRD and observed by SEM. The shape, size, and purity of the products strongly depended on the experimental conditions, which were classified according to the P-T equilibrium diagram for MgH$_2$. The diagram showed six distinct areas for the products MgH$_2$ and/or Mg having the following structures: fine and coarse powder, dendrite, root-like structure, straight and curved fibers, irregular bulk structure, and hexagonal and spherical structures. The diagram can be used quite effectively for controlling the shape of MgH$_2$ and/or Mg, and this may lay the foundation for the mass production of nano/microsized MgH$_2$/Mg for use in hydrogen storage or batteries.

KEYWORDS Hydrogen storage, magnesium hydride, nanostuctures, crystal growth, hydriding chemical vapor deposition
Introduction

Crystal growth of nano/micro materials has received increased attention because these materials exhibit unique properties and can be used in various applications.\(^1,2\) In this respect, the synthesis of Mg/MgH\(_2\) nano/microstructures could be of interest in the field of hydrogen storage and batteries.\(^3-7\) Magnesium hydride (MgH\(_2\)), which contains 7.6 mass% of hydrogen, is a promising candidate for hydrogen storage applications because of the relative abundance of Mg resources, low weight of Mg, and the high hydrogen content of MgH\(_2\).\(^8\) However, its applications have been limited by its high operation temperature of 300 °C at an equilibrium pressure of 0.1 MPa and the slow hydrogen adsorption kinetics of bulk Mg.\(^9\) To overcome these drawbacks, most studies have focused on the preparation of Mg/MgH\(_2\) nano/microstructures and nanocomposites.\(^3,4,10-20\) Mechanical milling of Mg/MgH\(_2\) with appropriate elements, alloys, or compounds is the most widely used method for producing such Mg-based nanomaterials.\(^3,16,17\) These materials have greatly contributed to elucidating the relationship between reactivity and nanostructure. Although some doping or alloying techniques can affect the desorption temperature, this always lowers the hydrogen storage capacity because of the additional weight. With the milling technique, the particle size of MgH\(_2\) can be reduced to several hundreds of nanometers while the grain size can be reduced to several tens of nanometers; however, in most cases, this is always accompanied by inhomogeneous size distributions, agglomeration, and impurities. Recently, Mg nanowires with diameters ranging from 30 to 170 nm were produced via a physical vapor-transport deposition method; these nanowires showed enhanced kinetics for hydrogen adsorption.\(^4\) Most significantly, the desorption energy of MgH\(_2\) (energy needed for the dissociation of MgH\(_2\) to Mg and H\(_2\); it is 74 kJ/mol-H\(_2\) for the bulk form), drastically decreased to 65.3 kJ/mol-H\(_2\) for nanowires with diameters of 30–50 nm. Hydriding chemical vapor deposition (HCVD)\(^18\) is another method used to produce MgH\(_2\) fibers (or wires in the nano/microscale) with high purity. These fibers were synthesized by depositing the vaporized Mg under H\(_2\) atmosphere, as expressed by the gas-gas reaction:
The as-prepared MgH₂ fibers showed excellent H₂ storage properties.¹⁹ MgH₂/Mg nano/microstructures are expected to depend on temperature and hydrogen pressure.²⁰,²¹ Historically, Dr. Ukichiro Nakaya of Hokkaido University, Sapporo, is world-famous for elucidating the relationship between the shape of snow crystals and the atmospheric conditions, i.e., temperature and supersaturation of the atmosphere.²² Weather conditions are now easily predicted thanks to the Nakaya diagram. In this respect, the synthesis of MgH₂/Mg nano/microstructures with shapes controlled under different temperature and hydrogen pressure may be of considerable interest for researchers in the field of hydrogen storage or batteries.²¹ The P-T diagram for MgH₂/Mg would be of great help in material design or mass production.

In this study, we carried out the controlled synthesis of MgH₂/Mg nano/microstructures. We succeeded in controlling the shapes (nanofibers, nanoparticles, microdendrites, irregular bulk, hexagonal microplates, and microspheres) and compositions of the products by adjusting the deposition temperature and H₂ pressure. The results were plotted on a thermodynamic P-T (pressure-temperature) diagram on basis of the dissociation of MgH₂, as shown in Figure S1:

\[
\text{MgH}_2 (s) \leftrightarrow \text{H}_2 (g) + \text{Mg} (s) \quad (2)
\]

Thermodynamically, the white area denotes the stable phase of MgH₂; the shadowed area indicates MgH₂ dissociating into Mg and H₂ under high temperatures. Theoretically, we should be able to produce MgH₂ in the MgH₂ stable area and Mg in the decomposition area. More details are presented in the following sections.
Experimental section

MgH$_2$/Mg products were prepared from commercially available Mg (purity 99.9%, particle size < 75 µm) under a highly pure H$_2$ atmosphere (99.99999%). The experimental setup was modified from ref. 21 as shown in Figure S2-(a): a cooler jacket running with cooled water was set around the left-hand flange of the Inconel tube reactor to produce a larger temperature distribution along the tube wall. A piece of stainless mesh (100 mesh, Φ0.10 × 100 × 220 mm, SUS304, Nilaco Ltd.) adhered along the tube wall was used as the substrate for collecting the products. Five grams of raw Mg were heated to vaporization at 600 ºC under 1, 2, 3, and 4 MPa of H$_2$; the reactants of H$_2$ and Mg vapor were deposited onto the cooled substrate and formed MgH$_2$/Mg products. Heating times of 7, 13, and 20 h were used; after several hours of heating, the reactor was cooled down to room temperature in about 1 hour by a fan, during which time the H$_2$ pressure was kept consistent with that during the heating process.

The temperature distribution along the inner top of tube wall (with the mesh on) was measured beforehand under different H$_2$ pressures of 1, 2, 3, and 4 MPa. The temperature measuring apparatus (see Figure S2-(c)) consisted of six thermocouples (K-type, Φ0.5 mm) with spacings of 1.5, 1.5, 1.0, 1.5, and 1.5 cm; by moving the slider fastened on the fixing device, we were able to measure the temperatures of different positions along the mesh (inner top of the tube wall). The temperature distribution is shown in Figure S3 as a function of distance from the inner surface of the left-hand flange.

Deposits with widths of 2 cm on the mesh corresponding to the inner top part of tube wall were collected for characterization. The as-prepared samples were characterized by powder X-ray diffraction (XRD, Rigaku Miniflex, CuKα) for composition analysis and scanning electron microscopy (SEM, JEOL, JSM-6360LA) for morphology observation. The sample preparation methods for XRD and SEM observations as well as the reusing treatment of the mesh substrate are shown in Figure S2-(b). After collecting the products, the mesh was dipped into an HCl (0.1 mol L$^{-1}$) solution for several minutes with ultrasonic vibration and washed with distilled water and ethyl alcohol for several times, after which the mesh substrate was finally reused.
Results and discussions

\( \text{MgH}_2/\text{Mg} \) nano.microstructures were synthesized using the hydriding chemical vapor deposition (HCVD) method by controlling the hydrogen pressure and deposition temperature. Figure 1 shows the images of the products, which are inserted in the P-T diagram of \( \text{MgH}_2 \), deposited on the mesh under different \( \text{H}_2 \) pressures for a heating time of 7 h. The four samples clearly showed the same boundary at the position of \( 4.3 \pm 0.1 \) cm distance from the left-hand flange (see Figure S4). By adjusting the temperature distribution (Figure S3), the product images were inserted into the P-T diagram of \( \text{MgH}_2 \) (Figure 1). On the right side of the boundary \( (4.3 \pm 0.1 \text{ cm}; \text{line b in Figure 1}) \), which is denoted as area 3 in Figure 1, the samples showed metallic shiny images, especially those deposited at low \( \text{H}_2 \) pressures; these may be metallic Mg. On the left side of the boundary, the samples showed a white color (area 2 in Figure 1), which can correspond to highly pure \( \text{MgH}_2 \); however, the samples were black on the low temperature side (area 1 in Figure 1), especially for those prepared at low \( \text{H}_2 \) pressures, which may indicate low purity of \( \text{MgH}_2 \). XRD patterns (Figure S5) confirmed these indicators: the metallic shiny substance deposited on the right side of the boundary (area 3 in Figure 1) was Mg, that was partially hydrogenated during the cooling process (in which the \( \text{H}_2 \) pressures were kept consistent with that in the heating process) after 7 h of heating; these samples showed higher intensity of \( \text{MgH}_2 \) at high \( \text{H}_2 \) pressures than that at low pressures. On the left side of the boundary, the white deposits (area 2 in Figure 1) showed highly pure \( \text{MgH}_2 \), especially those prepared under high \( \text{H}_2 \) pressures; however, far away from the boundary, at the low temperature side (area 3 in Figure 1), the samples showed decreasing purity of \( \text{MgH}_2 \) and were black in color (mixture of Mg and \( \text{MgH}_2 \)). This clearly shows that Mg was deposited exactly on the right side of the boundary because \( \text{MgH}_2 \) is decomposed at higher temperatures, as shown in Figure S1 (the shadowed area). Obviously, highly pure \( \text{MgH}_2 \) was deposited near the boundary on the left side since thermodynamically it is a stable \( \text{MgH}_2 \) area. However, a mixture of \( \text{MgH}_2 \) and Mg was also produced on the low temperature side despite being in the \( \text{MgH}_2 \) stable area. This is explained later by the hydrogenation kinetics of Mg; the growth mechanism is also discussed.
The measured boundary for the MgH$_2$ and Mg stable areas is plotted by the red solid line in Figure 1 and compared with the theoretical dissociation pressure for MgH$_2$, which is the black solid line. The measured boundary showed disagreement with the theoretical pressure as it was shifted to higher temperatures. The measured temperatures for separating the Mg and MgH$_2$ stable areas at 1, 2, 3, and 4 MPa were 396, 450, 481, and 501 °C, respectively, while the corresponding theoretical temperatures are 387, 427, 454, and 475 °C. Two reasons account for the shift: First, the fluctuation of the temperature distribution along the reactor tube wall caused by H$_2$ convection;$^{20}$ Second, since the products were cooled down to room temperature after several hours of heating while keeping the H$_2$ pressure constant, the original deposited Mg is partially hydrogenated during the cooling process. However, the measured and theoretical boundaries showed better agreement at the low H$_2$ pressure of 1 MPa (396 °C and 387 °C, respectively) than that at high H$_2$ pressures.

Scanning electron microscopy (SEM) was used to observe the morphology of the as-prepared samples at different H$_2$ pressures for different deposition temperatures. All of the results are summarized on the P-T diagram of MgH$_2$ shown in Figures 2 and 3 (Figure 3 is a simplified version of Figure 2; see also Figure S9 for more detailed information). Different shapes of crystals produced at different H$_2$ pressures and temperatures were classified into six distinct areas: (1) powder-shaped crystals at the nanoscale, where the powders are finer at low temperatures than that at high temperatures; (2) a mixture of powder, dendrite, root-like and curved coarse fibers at the microscale; (3) fiber-shaped crystals, that are curved and straight at the nano/microscale, in which the fibers are straighter and finer at higher pressures; (4) irregular bulk shapes at the microscale; (5) hexagonal shapes at the microscale; and (6) spherical shapes at the microscale.

Until now, we mainly concentrated on the results using a heating time of 7 h to summarize the relationship between the crystal morphology and deposition conditions, i.e. deposition temperature and H$_2$ pressure. We now demonstrate the kinetics and the growth mechanism here.
Figure 4 shows the images of the products deposited at 2 MPa with different heating times of 7, 13 and 20 h. As confirmed by the XRD analysis shown in Figure 5, prolonging the heating time caused the highly pure MgH$_2$ product area on the left side of the boundary (4.3 ± 0.1 cm) to shift to a lower temperature (left side). After 20 h of heating, all of the samples showed a single phase of MgH$_2$; we removed the subsequently deposited metallic shiny materials for 20 h of heating on the white product layer surface and the remaining product on the mesh was used for XRD analysis, which was compared with that of 7 and 13 h of heating; the reason is shown in the latter part about the metallic dendrite Mg crystals. Similar results for samples heated at 1 MPa are shown in the Supporting Information (Figures S6 and S7). Therefore, prolonging the heating time shifts line a in Figures 1 and 3 (only the composition information is considered), or for the boundary of areas 1 and 2, to the low temperature side; this enlarges the MgH$_2$ deposition area (area 2). This explains why we failed to produce highly pure MgH$_2$ in area 1 of Figure 1 with a heating time of 7 h, despite it being in the thermodynamically MgH$_2$ stable area.

The as-proposed gas-gas reaction at the deposition area shown in Eq. (1) should contain the following two steps in series:

\[
\text{Mg (g) } \rightarrow \text{Mg (s)} \quad \text{(3)} \quad R_1
\]

\[
\text{Mg (s) } + \text{H}_2 (g) \leftrightarrow \text{MgH}_2 (s) \quad \text{(4)} \quad R_2
\]

Eq. (3) is the condensation of the vaporized Mg, and Eq. (4) is the hydrogenation of the solid Mg. The reaction rates for them are $R_1$ and $R_2$, respectively. In the shadowed area of Figure S1 (the Mg stable area), only the condensation of the vaporized Mg occurred because MgH$_2$ is decomposed at high temperatures, where $R_1 >> R_2$; therefore, we produced Mg at the high temperature condition of area 3 in
Figures 1 and 3. In the white area of Figure S1 (the MgH$_2$ stable area), the hydrogenation of solid Mg (Eq. (4)) at high temperature and high H$_2$ pressure conditions had a larger reaction rate than that at low temperature and low H$_2$ pressure conditions; at the same time, the condensation of the vaporized Mg at low temperature side had a larger reaction rate than that at high temperature side; therefore, at low H$_2$ pressures of 1 and 2 MPa and at lower temperatures, the products showed a mixture of MgH$_2$ and Mg, where the reaction rate $R_1 > R_2$ and the solid Mg accumulated. However, prolonging heating time allowed the previously unhydrided Mg to be hydrogenated. The V-S (vapor-solid) growth mechanism was introduced to explain the growth of MgH$_2$ nanofibers because no catalyst was used during the HCVD process.$^{21}$ Combined with the two-step reaction in this study, the shapes of the deposited crystals must be determined by the first step of the Mg condensation. In the V-S mechanism, the shapes of the deposited crystals are affected by the concentration of the source vapor, deposition temperature (concentration of the source vapor and deposition temperature control the supersaturation degree of the source vapor), and deposition cooling rate. Various Mg structures, such as nanowires (curved and straight), spheres, flakes, rods, and sea urchin-like shapes, were successfully prepared by changing the temperature for Mg evaporation and the flow rate of Ar carrier gas in a physical vapor-transport deposition method.$^{4,5}$ The vapor source concentration and deposition temperature (and thus different levels of supersaturation) were also found to influence the morphology of MgO grown by the V-S method.$^{23,24}$ In our experiments, the Mg raw material was heated to vaporization in the evaporation area at 600 °C under H$_2$ pressures of 1, 2, 3, and 4 MPa. Two reactions are expected to occur in this area:

\[
\text{Mg (s) + H}_2\text{(g)} \leftrightarrow \text{MgH}_2\text{(s)} \quad (5)
\]

\[
\text{Mg (s)} \rightarrow \text{Mg (g)} \quad (6)
\]
Clearly, the concentration of Mg vapor supplied was higher at low H\textsubscript{2} pressures than that at high H\textsubscript{2} pressures. The results showed that in the MgH\textsubscript{2} stable area, a high H\textsubscript{2} pressure and temperature condition was advantageous for producing uniform and thin MgH\textsubscript{2} nanofibers. Fibrous highly pure MgH\textsubscript{2} was produced under 4 MPa H\textsubscript{2} at the temperatures near the theoretical dissociation temperature, where there was a large reaction rate due to a low concentration of Mg vapor and high H\textsubscript{2} pressure; and the reaction rate R\textsubscript{2} > R\textsubscript{1}, the MgH\textsubscript{2} nanofibers seemed to grow from the direct gas-gas reaction as shown in Eq. (1).

We observed a metallic shiny material deposited on the surface of the white MgH\textsubscript{2} near the boundary of 4.3 ± 0.1 cm at a heating time of 20 h under H\textsubscript{2} pressures of 1 and 2 MPa; the area is indicated by a rectangle in Figure S8. The metallic shiny material had various dendrite shapes similar to the dendrite Mg prepared in our previous study.\textsuperscript{21} Due to the long deposition time, the product layer grew thicker, and the temperature on the layer surface was higher than that on the mesh, which may shift to the MgH\textsubscript{2} decomposition area. This is also why the results after 7 h of heating were used to summarize the relationship between the crystal morphology and the deposition conditions for temperature and H\textsubscript{2} pressure.
Conclusions

In summary, we carried out the shape-controlled growth of MgH$_2$/Mg nano/microstructures by hydriding chemical vapor deposition (HCVD). We were easily able to control the shape of the products by adjusting the deposition temperature and H$_2$ pressure. The results were plotted on a thermodynamic P-T diagram for MgH$_2$. Different shapes of crystals having different compositions were prepared at different temperatures and pressures. The growth mechanism for the HCVD method was discussed both thermodynamically and kinetically. The results shown in the P-T diagram will allow us to determine the optimum conditions for synthesizing different shapes of products by HCVD, and this may lay the foundation for the mass production of nano/microsized MgH$_2$/Mg for use in hydrogen storage or batteries.
Acknowledgements

The authors would like to acknowledge Taiatsu Techno Co. Ltd for their technical support on improving the apparatus. We also thank Mr. G. Saito for his great help during the experiment.

Supporting Information Available: (1) Figure S1: Thermodynamic P-T diagram of MgH$_2$; (2) Figure S2: Schematic diagram for the preparation of MgH$_2$/Mg nano/microstructures; (3) Figure S3: Temperature distribution on the mesh at different H$_2$ pressures; (4) Figure S4: Images of the products deposited on the mesh at different H$_2$ pressures at a heating time of 7 h; (5) Figure S5: XRD patterns of the samples synthesized at different deposition temperature areas under different H$_2$ pressures at a heating time of 7 h; (6) Figure S6: Images of the products deposited on the mesh synthesized under 1 MPa H$_2$ at heating times of 7, 13, and 20 h; (7) Figure S7: XRD patterns of the samples synthesized at different deposition temperature areas under 1MPa H$_2$ at heating times of 7, 13 and 20 h; (8) Figure S8: Metallic shiny materials separated from the as-deposited white product; (9) Figure S9: Detailed morphology information of the deposited products at different deposition temperatures prepared at different H$_2$ pressures. This information is available free of charge via the Internet at http://pubs.acs.org/.
REFERENCES

Shape-controlled growth of MgH$_2$/Mg nano/microstructures via hydriding chemical vapor deposition (HCVD) was achieved by adjusting the deposition temperature and H$_2$ pressure. Different shapes of crystals having different compositions were prepared at different temperatures and pressures. The results were plotted on the thermodynamic P-T diagram of MgH$_2$, which allows us to determine the optimum conditions for synthesizing different shapes of products by HCVD.
Theoretical dissociation pressure of MgH$_2$
Figure 1. Deposited product images on the mesh inserted on the P-T diagram of MgH$_2$. These images were edited to adjust the temperature distribution and sample compositions (more information see Figure S3, Figure S4, and Figure S5). The products were synthesized under H$_2$ pressures of 1, 2, 3 and 4 MPa, respectively, at a heating time of 7 h. The black solid line is the theoretical dissociation pressure of MgH$_2$ as a function of temperature, and the red solid line was plotted using the experimental results. Area 1 is a mixture of MgH$_2$ and Mg; area 2 (between the two red lines) is a highly pure MgH$_2$ area; and area 3 is Mg. Prolonging the heating time shifts line a to low temperatures (left side) and enlarges the MgH$_2$ deposition area (area 2).
Figure 2. Morphology of the deposited products at different deposition temperatures and \( \text{H}_2 \) pressures inserted on the P-T diagram of MgH\(_2\). The black solid line shows the theoretical dissociation pressure of MgH\(_2\) as a function of temperature. The black dash lines enclose the measurable area in this experiment corresponding to the product images in Figure 1. (More detailed information about the morphology of the deposited products, see Figure S9)
Theoretical dissociation pressure of MgH$_2$.

Area 1: MgH$_2$ + Mg
Area 2: MgH$_2$
Area 3: Mg

H$_2$ pressure [MPa]

Temperature [°C]
Figure 3. Simplified morphology and composition distributions of the deposited products at different deposition temperatures and H\textsubscript{2} pressures plotted in the P-T diagram of MgH\textsubscript{2}. The composition distribution information is based on the results at a heating time of 7 h. The black solid line shows the theoretical dissociation pressure of MgH\textsubscript{2} as a function of temperature, and line b is plotted using the experimental results. The black dash lines enclose the measurable area in this experiment corresponding to the products images in Figure 1. Area 1 is a mixture of MgH\textsubscript{2} and Mg having powder, dendrite, root-like, and curved fibrous shapes. Area 2 is highly pure MgH\textsubscript{2} having curved and straight fiber shapes. Area 3 is Mg having irregular, hexagonal, and spherical shapes. When only the composition information is considered, prolonging the heating time shifts line a to low temperatures (left side) and enlarges the MgH\textsubscript{2} deposition area (area 2).
Figure 4. Images of the products deposited on the mesh synthesized under H$_2$ pressure of 2 MPa at different heating times of 7, 13, and 20 h. Insets show the XRD sample preparation and the composition distribution based on the XRD results in Figure 5.
Figure 5. XRD patterns of the samples synthesized at different deposition temperature areas under 2 MPa of H$_2$ at heating times of 7, 13 and 20 h. The sample numbers correspond to that in Figure 4. MgO peaks were due to exposure of the samples to the air during measuring, and the unhydrogenated Mg was partially oxidized.
Supporting information

Shape-controlled Growth of MgH$_2$/Mg Nano/Microstructures via Hydriding Chemical Vapor Deposition

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(6) Figure S6: Images of the products deposited on the mesh synthesized under 1 MPa H$_2$ at heating times of 7, 13, and 20 h
(7) Figure S7: XRD patterns of the samples synthesized at different deposition temperature areas under 1MPa H$_2$ with heating times of 7, 13, 20 h
(8) Figure S8: Metallic shiny materials separated from the as-deposited white product
(9) Figure S9: Detailed morphology information of the deposited products at different deposition temperatures prepared at different H$_2$ pressures
Figure S1. Thermodynamic P-T diagram of MgH₂ (Dissociation pressure of MgH₂ as a function of temperature). This diagram is calculated using HSC Chemistry, Version 5.1, based on the dissociation of MgH₂: MgH₂ (s) ↔ Mg (s) + H₂ (g).
(2).

(a) [Diagram showing experimental setup with labels: mesh, cooler, furnace, Mg powders, H\textsubscript{2} atmosphere, flange, pressure gauge, inlet, outlet, thermocouples, inner surface.]

(b) [Diagram showing washing process with labels: mesh, sticky carbon tape, SEM/XRD sample stage, washing, ultrasonic bath, 0.1M HCl, SEM observation, XRD characterization, product on mesh.]
Figure S2. (a) Schematic diagram of the whole experimental setup with the enlarged stainless mesh used;
(b) Schematic diagram of the preparation methods for XRD and SEM observations as well as the reusing treatment of the mesh substrate.
(c) Schematic diagram of the temperature measuring setup.
Figure S3. Temperature distribution on the mesh adhered along the tube wall under H\textsubscript{2} pressures of 1.0, 2.0, 3.0, and 4.0 MPa, respectively. The top of tube with the mesh on was measured.
Figure S4. Images of the products deposited on the mesh under H\textsubscript{2} pressures of 1, 2, 3, and 4 MPa, respectively, at a heating time of 7 h. Insets show the XRD samples preparation. The deposits on the mesh corresponding to the central top of the tube wall were collected.
(5).

1 MPa-7h

S9

S8

S7

S6

S5

S4

S3

S2

S1

Intensity [ a.u. ]

2θ [ ° ]

2 MPa-7h

S7

S6

S5

S4

S3

S2

S1

Intensity [ a.u. ]

2θ [ ° ]
Figure S5. XRD patterns of the samples synthesized at different deposition temperature areas under 1, 2, 3, and 4 MPa of H$_2$, respectively, at a heating time of 7 h; the sample numbers correspond to that in Figure S4. The peaks of MgO appeared in the XRD patterns, this is due to the exposure of these samples to the air, and the unhydrided Mg was partially oxidized, especially in the low deposition temperature and low H$_2$ pressure areas where the deposited products were fine powders.
Figure S6. Images of the products deposited on the mesh synthesized under H$_2$ pressure of 1 MPa at different heating times of 7, 13, and 20 h. Insets show the XRD samples preparation and the composition distribution based on the XRD results in Figure S7.

More discussion about the results under H$_2$ pressure of 1 MPa can be found in “Chunyu Zhu et al., Investigation of MgH$_2$ production at low H$_2$ pressure via hydriding chemical vapor deposition. Proceeding of Renewable Energy 2010, Yokohama, Japan.”
Figure S7. XRD patterns of the samples synthesized at different deposition temperature areas under 1 MPa of H\textsubscript{2} with heating times of 7, 13, and 20 h. The sample numbers correspond to that in Figure S6. MgO peaks were due to exposure of the samples to the air during measuring.
Metallic shiny Mg deposited under 1 MPa with a heating time of 20 h

The dendrite shiny crystals deposited on the surface of the white product.

Figure S8. Metallic shiny materials separated from the as-deposited white product (MgH$_2$) near the boundary of 4.3 ± 0.1 cm. The heating time was 20 h at 1 MPa H$_2$. The one at 2 MPa with heating time of 20 h have the similar dendrite crystals.
SEM images of the metallic shiny material
Figure S9. Detailed morphology information of the deposited products at different deposition temperatures prepared at different H\textsubscript{2} pressures.
1 MPa-product image

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 cm
1 MPa-SEM
1 MPa-SEM
2 MPa-product image

cm
1 MPa-SEM

2 MPa-SEM

3 MPa-SEM

4 MPa-SEM

5 MPa-SEM

6 MPa-SEM

7 MPa-SEM

8 MPa-SEM

9 MPa-SEM
3 MPa-product image
3 MPa-SEM
4 MPa-product image
4 MPa-SEM
4 MPa-SEM