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Author(s)	Zhu, Chunyu; Sakaguchi, Norihito; Hosokai, Sou et al.
Citation	International Journal of Hydrogen Energy, 36(5), 3600-3605 https://doi.org/10.1016/j.ijhydene.2010.12.017
Issue Date	2011-03
Doc URL	https://hdl.handle.net/2115/45175
Type	journal article
File Information	IJHE36-5_3600-3605.pdf



In situ Transmission Electron Microscopy Observation of the Decomposition of MgH_2 Nanofiber

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ABSTRACT:

In this paper, we presented an investigation of the phase transformation of MgH_2 to Mg, in which a sample of a single-crystal MgH_2 nanofiber was prepared by hydriding chemical vapor deposition (HCVD) and observed by in situ (high-resolution) transmission electron microscopy (TEM). The results indicated that the orientation relationship between MgH_2 and Mg during the phase change was: one of the zone axis of MgH_2 $\langle 110 \rangle$ parallel to Mg $[0001]$ zone axis, or one of the plane $\{110\}$ of MgH_2 parallel to the basal plane of Mg (0001). On the basis of the obtained results, we proposed a structural model for the phase change of MgH_2 to Mg.

Keywords: Hydrogen storage, Magnesium hydride, nanofiber, hydriding chemical vapor deposition, TEM

1. INTRODUCTION

Magnesium is a promising candidate for solid hydrogen storage owing to its abundance, low cost, reversibility, high gravimetric H₂ density of 7.6 mass %, and high volumetric H₂ density of 110 g/L hydrogen density. However, magnesium, or magnesium hydride, has limited its practical applications because of the high operation temperature and the slow hydrogen adsorption kinetics. [1, 2] To overcome these drawbacks, most studies focus on the preparation of Mg-rich alloys and composites. [3, 4] However, this causes lowering the H₂ storage capacity due to the added weight of the elements or compounds. Another solution is to reduce the size of the Mg/Mg-based materials to the nano-scale. In order to manufacture micro/nano-structured Mg or MgH₂ and their composites many processes, such as high-energy ball milling of MgH₂ or MgH₂-based composites [3-5], magnetron sputtering for Mg thin films, [6] physical vapor-transport deposition (PVD) of Mg nanowires, [7] and hydriding chemical vapor deposition (HCVD) of MgH₂ nanofibers, [8-10] have been used. The as-prepared Mg nanowires by the PVD method having diameters ranging from 30 to 170 nm exhibit enhanced hydrogen adsorption kinetics. Most significantly, the dissociation energy for the transformation of MgH₂ to Mg and H₂ decreases drastically from 74 kJ/mol-H₂ for bulk to 65.3 kJ/mol-H₂ for nanowires with diameters of 30–50 nm.[7]

The HCVD method can be used to manufacture highly pure single-crystal nanofibers of MgH₂ on the nano/micro-scale. It has been reported that the as-prepared MgH₂ nanofibers exhibit excellent H₂ adsorption properties. [11] However, the mechanism underlying the dehydrogenation of the MgH₂ nanofibers are still not understood completely. Therefore, the purpose of this study is to observe the phase change of MgH₂ nanofiber prepared by HCVD to Mg via in situ (high-resolution) TEM, in which a structural model for elucidating the phase transformation of MgH₂ to Mg during the dehydrogenation is proposed.

2. EXPERIMENTAL

MgH₂ nanofibers were prepared by a gas-gas reaction ($\text{H}_2(\text{g}) + \text{Mg}(\text{g}) \rightarrow \text{MgH}_2(\text{s})$), i.e. the HCVD method, as described elsewhere. [8, 9, 11] 10 g of commercially available Mg powder (purity: 99%; particle size: < 75 μm) was placed in an Inconel tube and heated to vaporize in an H₂ atmosphere (purity: 99.99999%) at 4.0 MPa and at a temperature of 600 °C for 20 hours. The reactants, namely, the H₂ and Mg in vapor form, were deposited on the cooled Inconel flange substrate of the reactor at a temperature of 400 ~ 500 °C to form MgH₂ nanofibers. Due to the sensitivity of MgH₂ to a moisture atmosphere, the as-prepared samples were stored in a dry Argon atmosphere.

The decomposition of MgH₂ nanofibers was induced by an electron beam, and the phase transformation of MgH₂ to Mg was observed by in-situ (high-resolution) transmission electron microscopy ((HR)-TEM, 200 kV, JEM-2010). A low-density electron beam was used to investigate the hydride and a high-density electron beam was used to decompose the hydride. A series of TEM bright-field (BF) images and selected area electron diffractions (SAEDs), before, during, and after decomposition, were obtained at the same area of an MgH₂ nanofiber. The observation for one nanofiber was completely in approximately ten minutes, and the MgH₂ nanofiber decomposed very quickly when it was irradiated with a high-density electron beam.

The MgH₂ samples were dispersed on carbon-collodion-coated copper grids in a vial by shaking it vigorously for TEM observation. The HR-TEM images were analyzed using the software Digital Micrograph (Gatan, Inc.). All the crystal structures were drawn using Crystal Studio (Version 4.0, Crystal System Co. Ltd.).

3. RESULTS AND DISCUSSION

3.1 Crystal structures of Mg and MgH₂

Magnesium has a hexagonal-close-packed (hcp) structure (space group of P6₃/mmc) with lattice parameters of $a = b = 3.21 \text{ \AA}$ and $c = 5.21 \text{ \AA}$. [12] On the other hand, magnesium hydride has a tetragonal rutile (P4₂/mmn) structure with $a = b = 4.50 \text{ \AA}$ and $c = 3.01 \text{ \AA}$. Figure 1 shows the unit cell images of MgH₂ and Mg. Insets of Figure 1 show the atomic arrangement for MgH₂ (110) and Mg (0001), respectively.

3.2 TEM decomposition of the MgH₂ nanofiber

Figure 2 shows a sequence of images (a, c, and e) and the corresponding SAED patterns (b, d and f) of an MgH₂ nanofiber at different stages of decomposition induced by a TEM electron beam. Image (a) and SAED pattern (b) clearly show that before decomposition, the nanofiber has a single phase, namely, that of tetragonal rutile MgH₂, as seen from the [110] zone axis. Image (c) and SAED pattern (d) show both the phases, namely, an MgH₂ phase and an Mg phase. After being exposed to a high-density electron beam, the MgH₂ nanofiber decomposed to Mg with a greater speed. Image (e) shows the completely dehydrogenated MgH₂ nanofiber and the SAED pattern (f) indicate the hexagonal Mg with [0001] zone. Images (g) and (h) show a high-resolution TEM image of Mg and a simulated lattice image obtained from the digital diffractogram as shown in (g), respectively. This lattice image of (h) indicates Mg planes of {10-10}.

Here, we index the MgH₂ SAED pattern from the [110] zone axis, as shown in Figure 2 (b), for discussing the orientation relationship of MgH₂ with Mg. It is also reasonable to index it as the [-110], [1-10] or [-1-10] zone axis, since these axes are in the same general direction of <110> having the same properties in each direction. For the hexagonal diffraction pattern of Mg from the [0001] zone axis, one can freely change the order of the face indices at the six vertices since they are on the same general face of {10-10}, and one example is shown in Figure 2 (f). It should be noted that different

indexing methods lead to different expressions for the orientation relationship between MgH_2 and Mg. Thus, we were careful during the comparison of the obtained results with those from other studies. Here, we conclude that the relationship is: one of the zone axis of MgH_2 $\langle 110 \rangle$ parallel to Mg $[0001]$ zone axis, or one of the plane $\{110\}$ of MgH_2 parallel to the basal plane of Mg (0001).

Figure 3 shows the results of the careful observation of the orientation relationship via the high-resolution TEM technique. Figure 3 (a) is a typical TEM image of an MgH_2 nanofiber which is partially decomposed, and Figures 3 (b) and (c) show the corresponding SAED pattern indicating both the phases of MgH_2 and Mg; this diffraction pattern is the same as that in Figure 2 (d). Figure 3 (d) is the HRTEM image of the same fiber of Figure 3 (a). Figure 3 (e) is the digital diffractogram based on Fast Fourier Transform (FFT) from the selected dash line area in (d), which shows the two phases of MgH_2 and Mg. Figures 3 (f) and (g) are the simulated diffraction pattern and lattice image of the both phases of MgH_2 and Mg based on the digital diffractogram of Figure 3 (e). By masking the diffraction spots of the MgH_2 phase, the simulated diffraction pattern of Mg $[0001]$ and lattice image were shown in Figures 3 (h) and (i). Conversely, by masking that of Mg phase, the simulated diffraction pattern of MgH_2 $[110]$ and lattice image were presented in Figures 3 (j) and (k).

Table 1 summarizes the results of previous studies together with those of this study. Paik B. et al. [13] observed the phase change of MgH_2 to Mg by using commercial MgH_2 powder in TEM. They obtained a series of diffraction patterns of MgH_2 , which were subsequently transformed to those of Mg under irradiation by an electron beam, and summarized the relationship as $\text{MgH}_2[001] \parallel \text{Mg}[-2110]$ and $\text{MgH}_2(-110) \parallel \text{Mg}(0001)$. Bokhonov B. et al. [14] observed the orientation relationship of MgH_2 (110) parallel to Mg (0001) by using single crystals of MgH_2 whiskers. These results are the same as this study with the basal plane of Mg (0001) is parallel to one of the plane $\{110\}$ for MgH_2 . Schober T. [15] prepared a thin Mg disc and then hydrogenated it for TEM observation. He summarized the relationship as $\text{MgH}_2(100) \parallel \text{Mg}(0001)$ and $\text{MgH}_2[001] \parallel \text{Mg}[-1-120]$, which is different from this study. Kelekar et al. [16] reported various orientation relationships between MgH_2 and Mg according to an XRD analysis, in which epitaxial Mg thin films were deposited on different substrates and were then hydrogenated. When an Al_2O_3 substrate was used, the relationship was $\text{MgH}_2(110)[001] \parallel$

Mg(001)[100]. However, when a LiGaO₂ substrate was used, the relationship was MgH₂(200)[001] // Mg(110)[-111].

3.3 Structural model for the phase transformation: MgH₂ to Mg

Magnesium has an hcp structure with the atom stacking sequence of ABABAB.... Figure 4 (a) shows an image for the hcp stacking and Figure 4 (b) shows the atomic arrangement of MgH₂ and Mg viewed from the [110] and [0001] directions, respectively. Figures 4 (c) and (d) show a hexagonal unit cell for Mg and an analogous hcp unit cell for MgH₂ viewed from the [110] direction. For the analogous hcp unit cell of MgH₂, we calculate the cell parameters: $a' = c = 3.01 \text{ \AA}$, $b' = 3.52 \text{ \AA} = 0.5 * (a^2 + b^2 + c^2)^{1/2}$, and $c' = 6.36 \text{ \AA} = 2 d_{(110)} = (a^2 + b^2)^{1/2}$. Next, we schematically show how MgH₂ transforms to Mg during dehydrogenation. As shown in Figures 4 (c) and (d), first, on the two layers of A, the value of a' for MgH₂ (3.01 Å) prolongs to Mg for $a = 3.21 \text{ \AA}$, and b' of MgH₂ (3.52 Å) shortens to Mg for $b = 3.21 \text{ \AA}$; at the same time, the angle of 64.7° shrinks to fit 60°. Along the c' -axis ($c' = 6.36 \text{ \AA}$), the two layers of A move toward each other to form Mg with $c = 5.21 \text{ \AA}$. Finally, on layer B, the atom from the (1/2, 1, 1/2) site of analogous hcp-MgH₂ will move to (1/3, 2/3, 1/2) of Mg. This scheme, presented in Figure 4, shows the movement of the Mg atoms of MgH₂ after losing hydrogen during the decomposition. Conversely, in the hydrogenation process, we believe that the Mg atoms move in the opposite directions for accepting hydrogen.

3.4 CONCLUSIONS

We investigated the phase transformation of MgH_2 to Mg by in situ (high-resolution) transmission electron microscopy using a sample of MgH_2 single-crystal nanofibers prepared by hydriding chemical vapor deposition. An electron beam induced the decomposition of MgH_2 to Mg. The results indicated the orientation relationship between MgH_2 and Mg during the phase change was one of the zone axis of MgH_2 $\langle 110 \rangle$ parallel to Mg $[0001]$ zone axis, or one of the plane $\{110\}$ of MgH_2 parallel to the basal plane of Mg (0001). On the basis of these results, we proposed a structure model for the phase transformation of MgH_2 to Mg.

Acknowledgements

The authors would like to thank Mr. G. Saito and Mr. K. Ohkubo for their technical support on TEM observation.

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Table 1. Comparison of the orientation relationship between MgH₂ and Mg during phase transformation, derived by different researches.

<i>Materials</i>	<i>Preparation method</i>	<i>Observation method</i>	<i>Orientation relationship</i>	<i>Ref.</i>
HCVD MgH ₂ nanofibers	MgH ₂ Nanofibers prepared by hydriding chemical vapor deposition (HCVD)	(HR)TEM	(110)MgH ₂ //(0001)Mg	This study
MgH ₂ powder (purity 95%)	Commercial product	TEM (200 kV)	[001]MgH ₂ //[-2110]Mg (-110)MgH ₂ //(0001)Mg	Paik B. et al. [13]
MgH ₂ whisker	MgH ₂ whiskers formed on the surface of Mg spheres hydrided at 630 K and 1.6 MPa	TEM	(110)MgH ₂ //(0001)Mg	Bokhonov B. [14]
MgH ₂ disc	Mg discs hydrided at 270 °C and 5*10 ⁶ Pa	TEM (120 kV)	[001]MgH ₂ //[-1-120]Mg (100)MgH ₂ //(0001)Mg	Schober T. [15]
Epitaxial Mg (001) thin films	Mg thin film formed on (001) Al ₂ O ₃ substrate, then hydrided at 373 K and 0.6 MPa	XRD	[001]MgH ₂ //[100]Mg (110)MgH ₂ //(001)Mg	Kelekar R. [16]
Epitaxial Mg (110) thin films	Mg thin film formed on (320) LiGaO ₂ substrate, then hydrided at 373 K and 0.6 MPa	XRD	[001]MgH ₂ //[-111]Mg (200)MgH ₂ //(110)Mg	Kelekar R. [16]

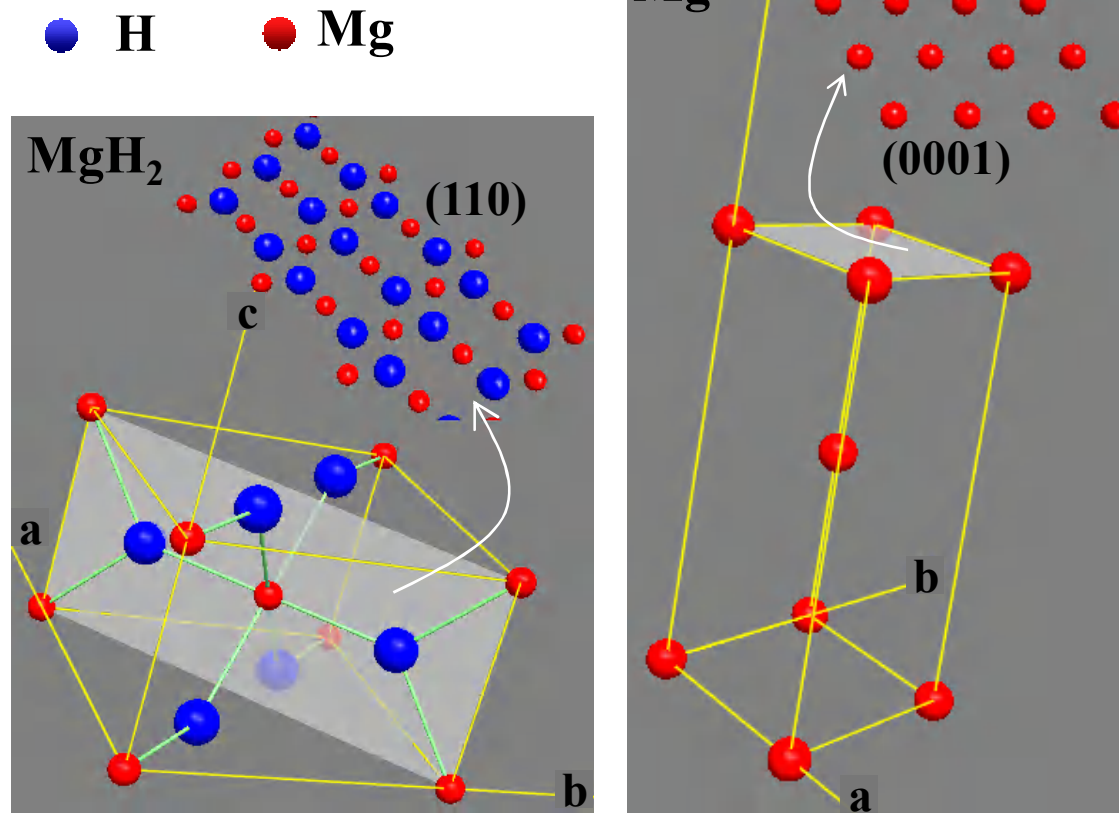


Figure 1. Unit cells of MgH_2 and Mg . Cell parameters for MgH_2 are $a = b = 4.50 \text{ \AA}$, $c = 3.01 \text{ \AA}$; cell parameters for Mg are $a = b = 3.21 \text{ \AA}$, $c = 5.21 \text{ \AA}$. Insets show the atomic arrangement on MgH_2 (110) and Mg (0001) , respectively.

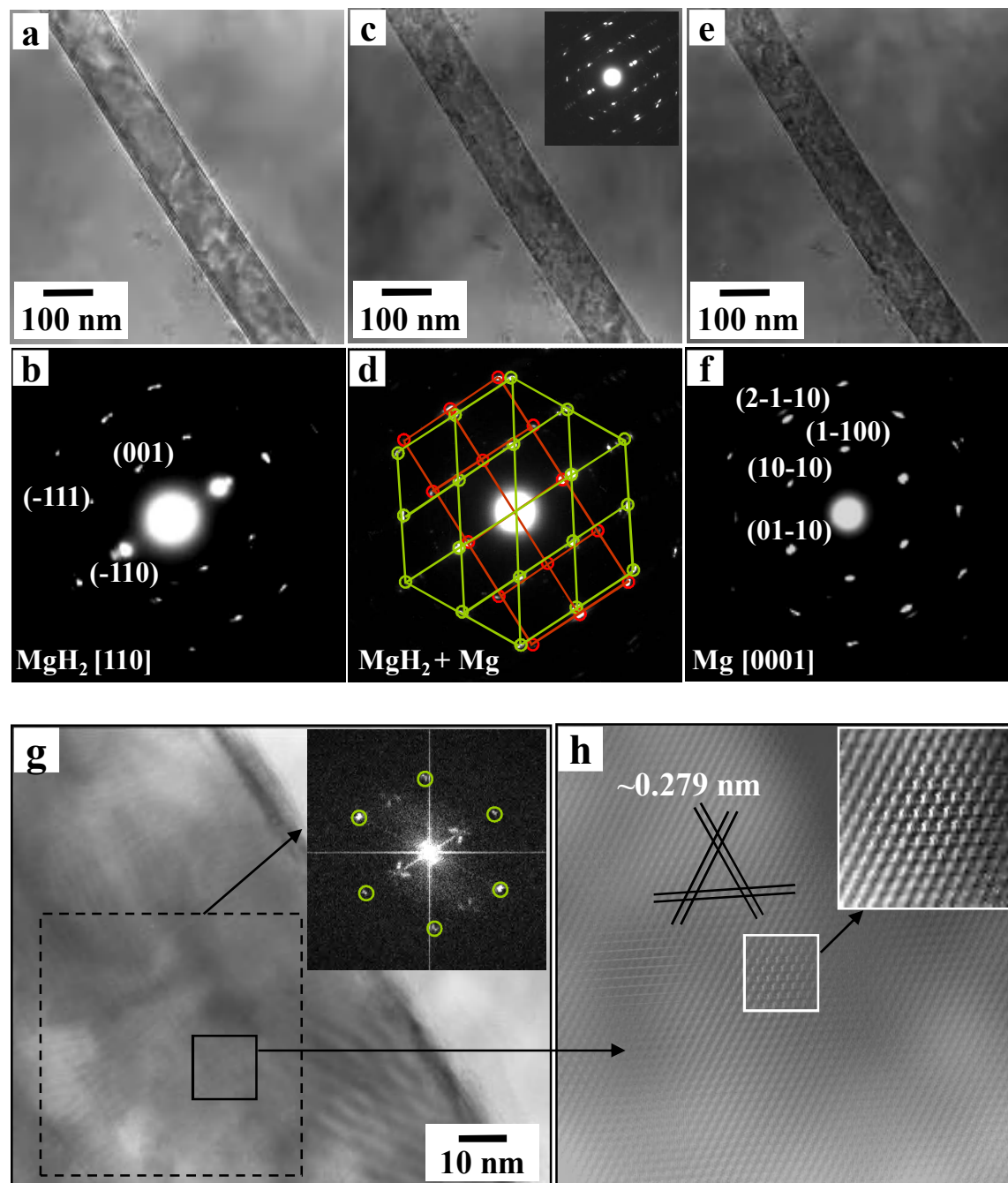


Figure 2. A sequence of images (a, c and e) and SAED patterns (b, d and f) of an MgH_2 nanofiber at different stages of decomposition induced by an electron beam. (a, b) single phase of MgH_2 ; (c, d) both phases of MgH_2 and Mg; (e, f) strong reflection of Mg. (g) HRTEM image of the decomposed nanofiber after (e) ; the inset is the digital diffractogram based on Fast Fourier Transform (FFT) from the selected dash line area. (h) is the simulated lattice image obtained from the digital diffractogram in (g) showing Mg planes of $\{10\text{-}10\}$. Red cycles represent the diffraction spots of MgH_2 and the green ones are Mg.

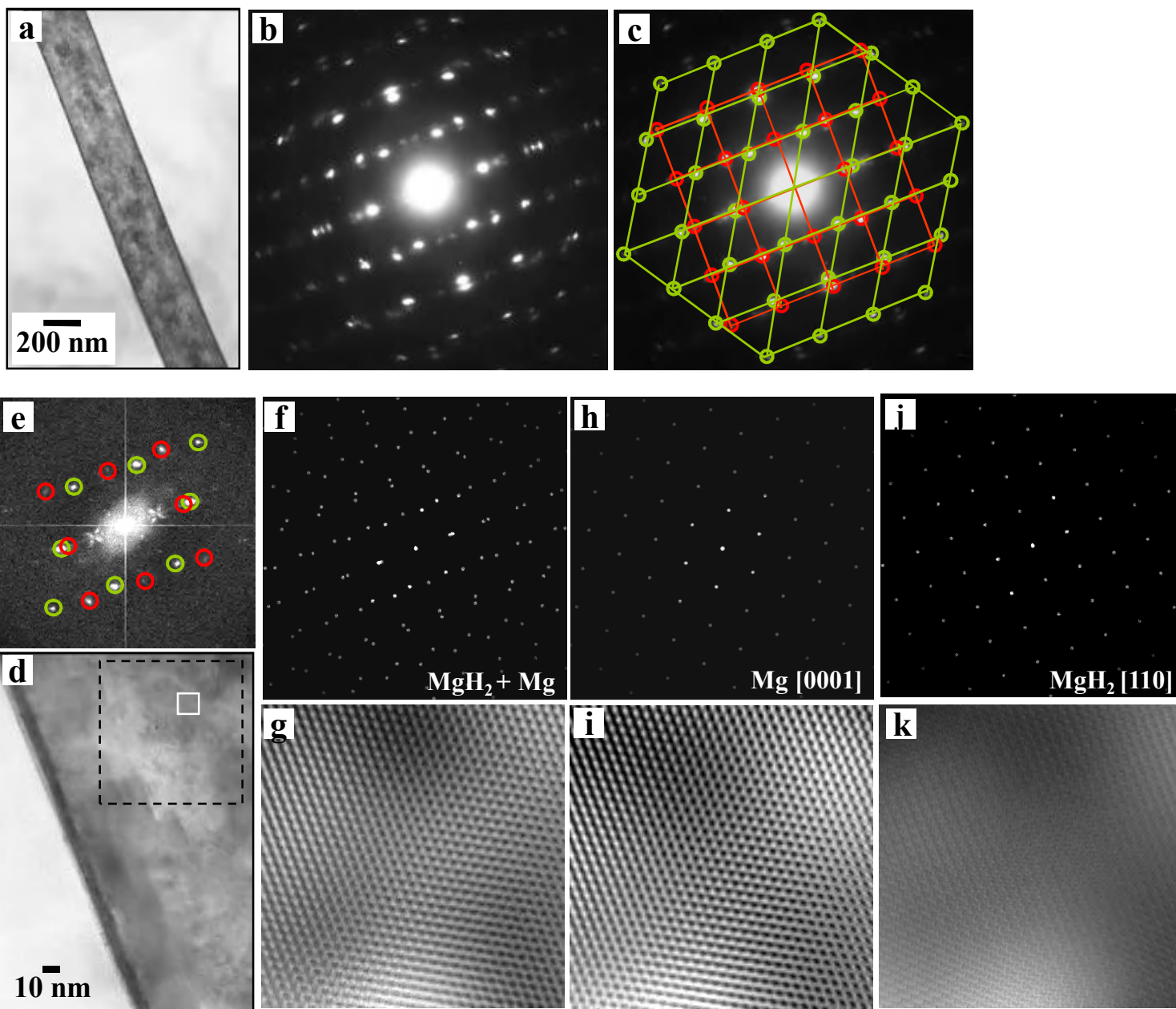


Figure 3. Typical (high resolution) TEM images (a, d) and SAED pattern (b and c, c is the same pattern of b) showing both phases of MgH_2 and Mg during decomposition. (e) is the digital diffractogram based on Fast Fourier Transform (FFT) from the selected dash line area in (d); this pattern shows both phases of MgH_2 and Mg corresponding to that in (b, c). (f, g) are the simulated diffraction pattern and lattice image showing both phases of MgH_2 and Mg obtained from the FFT digital diffractogram. (h, i) are the simulated diffraction pattern and lattice image of Mg by masking the diffraction of MgH_2 in (e). (j, k) are the simulated diffraction pattern and lattice image of MgH_2 by masking the diffraction of Mg in (e). Red cycles represent the diffraction spots of MgH_2 and the green ones are Mg.

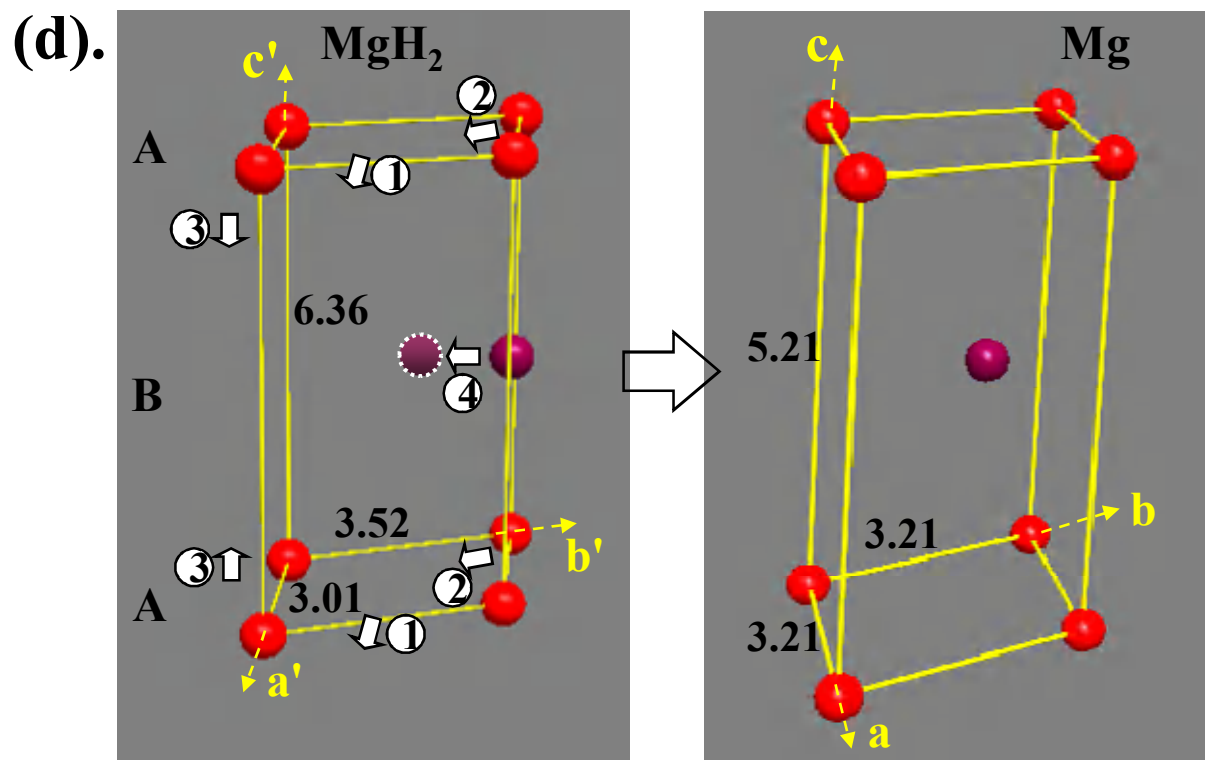
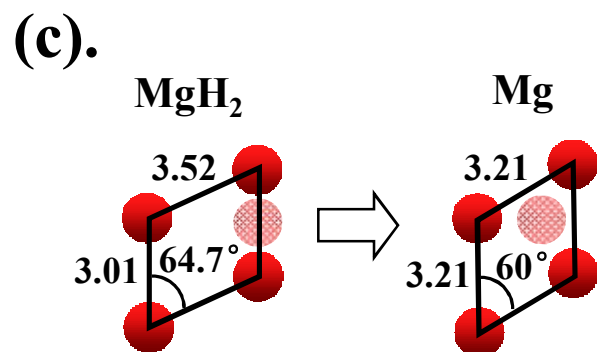
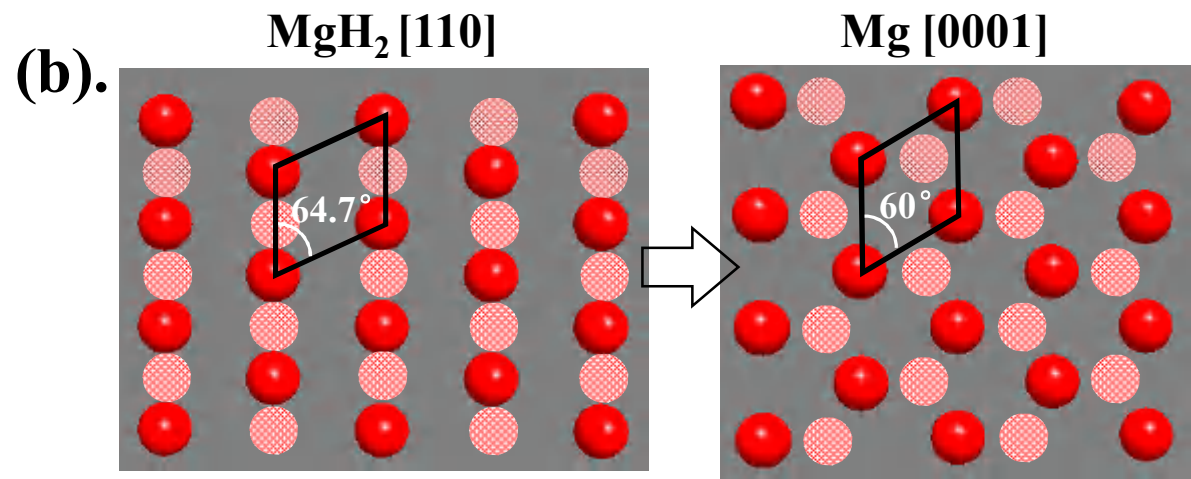
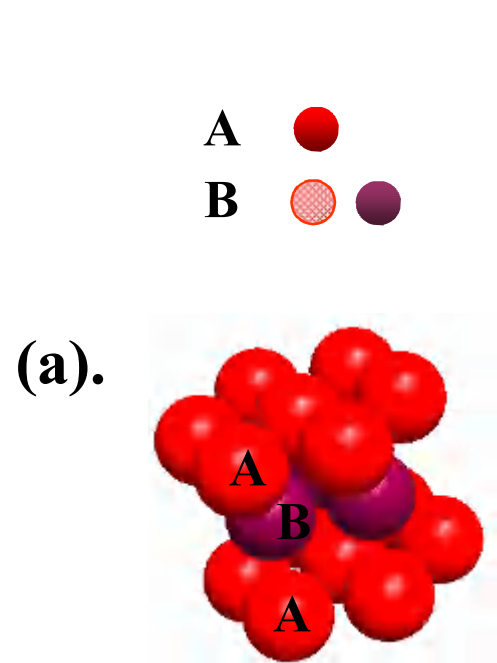


Figure 4. (a). Image for the hcp stacking, ABABAB...

(b). Atomic arrays of MgH_2 and Mg from $[110]$ and $[0001]$ view, respectively.

(c) and (d). The hexagonal unit cell for Mg and the analogous hcp unit cell for MgH_2 viewed from $[110]$ direction, the H atom in MgH_2 is neglected, (c) is the projection view down $\text{MgH}_2[110]$ and $\text{Mg}[0001]$, (d) is the perspective view.

For the analogous hcp unit cell of MgH_2 , $a' = c = 3.01$, $b' = 3.52 = 0.5 * (a^2 + b^2 + c^2)^{1/2}$, $c' = 6.36 = 2 d_{(110)} = (a^2 + b^2)^{1/2}$. For Mg, $a = b = 3.21$, $c = 5.21$. All distances are expressed in Å.