



Study on reaction mechanism of dehydrogenation of magnesium hydride by in situ transmission electron microscopy

Shigehito Isobe, Akifumi Ono, Hao Yao, Yongming Wang, Naoyuki Hashimoto, and Somei Ohnuki

Citation: Applied Physics Letters **96**, 223109 (2010); doi: 10.1063/1.3442910 View online: http://dx.doi.org/10.1063/1.3442910 View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/96/22?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

Transmission electron microscopy study on Co/Fe interdiffusion in SmCo5/Fe and Sm2Co7/Fe/Sm2Co7 thin films J. Appl. Phys. **110**, 053914 (2011); 10.1063/1.3634063

Metal-hydride transformation kinetics in Mg nanoparticles Appl. Phys. Lett. **94**, 041918 (2009); 10.1063/1.3077186

Gas-phase synthesis of magnesium nanoparticles: A high-resolution transmission electron microscopy study Appl. Phys. Lett. **89**, 161914 (2006); 10.1063/1.2358860

In situ high-resolution transmission electron microscopy study of interfacial reactions of Cu thin films on amorphous silicon Appl. Phys. Lett. **88**, 083117 (2006); 10.1063/1.2179143

Deuterium storage in nanocrystalline magnesium thin films J. Appl. Phys. **95**, 1989 (2004); 10.1063/1.1637953

Confidently measure down to 0.01 fA and up to 10 PΩ Keysight B2980A Series Picoammeters/Electrometers

Study on reaction mechanism of dehydrogenation of magnesium hydride by *in situ* transmission electron microscopy

Shigehito Isobe,^{a)} Akifumi Ono, Hao Yao, Yongming Wang, Naoyuki Hashimoto, and Somei Ohnuki

Graduate School of Engineering, Hokkaido University, N-13, W-8, Sapporo 060-8278, Japan

(Received 6 April 2010; accepted 10 May 2010; published online 2 June 2010)

In situ observation on dehydrogenation of MgH₂ was performed by using transmission electron microscope (TEM). The dehydrogenation of MgH₂ with 1 mol % Nb₂O₅ and formation of nanosized Mg particles were observed at 150 °C. Nb₂O₅ was not confirmed in diffraction patterns and TEM images probably due to wide dispersion. On MgH₂ with 10 mol % Nb₂O₅, the high resolution TEM could recognize the dehydrogenation at the interface between MgH₂ and Nb₂O₅, proceeding with increasing temperature. This suggests that hydrogen atoms could diffuse from MgH₂ phase to the interface between Mg and Nb₂O₅, resulting in formation of hydrogen molecules at the interface. © 2010 American Institute of Physics. [doi:10.1063/1.3442910]

Mg has been regarded as a promising candidate for a base metal of hydrogen storage alloys, which have large capacity for hydrogen storage.¹⁻³ However, one of disadvantages is its slow reaction speed of hydrogenation and dehydrogenation. Recently, it has been suggested that oxide catalyst is effective for improving the hydrogenation and dehydrogenation kinetics of Mg. Barkhordarian et al. reported that Nb₂O₅ had the best effect on the hydrogen storage properties of Mg and MgH₂ as an oxide catalysts.⁴⁻⁶ Hanada et al. made some composite materials of MgH₂ catalyzed with transition metals and oxides by ball milling method, and reported that MgH₂ with 1 mol % of Nb₂O₅ has superior dehydrogenation characteristics.^{7–9} However, the detail of the catalytic reaction has not been understood yet. In this study, the change in the high resolution image before and after dehydrogenation was observed by using with TEM to examine the details of the catalytic reaction.

In this study, two kinds of samples with 1 and 10 mol % of Nb₂O₅ were prepared. For MgH₂ catalyzed with 1 mol % Nb₂O₅, MgH₂ powder (Alfa Aesar), and Nb₂O₅ powder (mesoporous: Sigma-Aldrich) were ball-milled under the hydrogen atmosphere of 1.0 MPa for 20 h. On the other hand, for

MgH₂ catalyzed with 10 mol % Nb₂O₅, MgH₂ powder, and Nb₂O₅ powder (single-crystalline: Kojundo chemical Laboratory) were mixed by agate mortar in a glovebox filled with Ar gas. The samples were handled without exposure to air in whole process. The sample powder was placed on a microgrid and the grid was set into a heating specimen holder in the glove box under Ar atmosphere. The heating specimen holder was put into a plastic bag under Ar atmosphere and loaded into TEM equipment in order to prevent the oxidation. The samples were observed from room temperature to 200 °C by using a TEM (JEOL-2010; 200 kV), and high resolution images of a 10 mol % catalyzed sample were obtained by using high voltage electron microscope (HVEM, JEM-ARM1300; 1250 kV). With respect to temperature control for in situ TEM observation, the temperature was rapidly raised up and kept at 100, 150, or 200 °C. The TEM images were analyzed by the selected area electron diffraction pattern (SADP), fast Fourier transformation (FFT), and inverse fast Fourier transformation (IFFT).

At the first step, observation by using a conventional TEM (200 kV) was carried out for MgH_2 catalyzed with 1 mol % Nb_2O_5 , which showed a remarkable catalytic effect.¹⁰



FIG. 1. BF images and diffraction pattern of 1 mol % catalyzed sample at room temperatures, 150 and 200 °C.

^{a)}Electronic mail: isobe@eng.hokudai.ac.jp.



FIG. 2. BF image (a), FFT (b), and IFFT (c) from 10 mol % catalyzed sample at room temperature.

Fig. 1 shows the bright field (BF) images and SADP of MgH₂ catalyzed with 1 mol % Nb₂O₅ at RT, 150 and 200 °C. In case of RT, the diffraction rings and patterns of MgH₂ and MgO were confirmed. MgO could be considered as an impurity in the starting material of MgH₂. At 150 °C, the diffraction ring of MgH₂ became weak and the diffraction ring of Mg appeared. Therefore, it was confirmed that the decomposition of MgH₂ and the formation of Mg started from around 150 °C. In the case of 200 °C, the diffraction ring of MgH₂ almost disappeared and the Debye ring of Mg developed, meaning that the Mg crystal was formed with several 10 nm in size. On the other hand, Nb₂O₅ was not identified by both BF images and SADP. In BF images, the shape of sample hardly changed while the contrast became weak with increasing temperature, indicating that the density of the particle decreased due to formation of voids.

In order to identify microstructure of interface between MgH₂ and Nb₂O₅, MgH₂ catalyzed with 10 mol % Nb₂O₅ was observed by using high resolution microscopy with HVEM (1250 kV). On the desorption kinetics, the dehydrogenation characteristics of the MgH₂+1 mol % Nb₂O₅ is superior to that of MgH₂+10 mol % Nb₂O₅ due to a larger amount of interface volume between MgH₂ and catalyst. Figure 2 shows (a) BF image, (b) FFT image, and (c) IFFT image at RT. As shown in Fig. 2(a), it was confirmed that upper and bottom parts are MgH₂ and Nb₂O₅, respectively. Meanwhile Mg formation is confirmed near the interface. Figures 2(b) and 2(c) are FFT and IFFT images from square in (a), showing phases of MgH₂ and Mg. It was indicated that the initial decomposition from MgH₂ to Mg occurred at the interface between MgH₂ and Nb₂O₅ even at RT. The reason why the decomposition started even at RT was probably due to an effect of electron-beam irradiation. Here, the effect of electron-beam irradiation on the decomposition should be considered. By electron-beam irradiation, the temperature would be locally increased. The decomposition could be caused by this local heating. However, despite the electron-beam irradiation could affect the entire sample; the results showed that Mg phase appeared at the interface. From this consideration, it can be recognized that the decomposition started at the interface due to the catalytic effect. The size of Mg phase, as shown in the dotted line in Fig. 2(a) was approximately 60 nm. Figure 3 shows BF image and related FFT and IFFT images at 100 and 200 °C. The Mg phase grew up with increasing temperature. Conclusively, we



FIG. 3. BF image (a), FFT (b), and IFFT (c) from 10 mol % catalyzed sample heated to 100 $^{\circ}$ C BF image (d), FFT (e), and IFFT (f) from 10 mol % catalyzed sample heated to 200 $^{\circ}$ C.

interface between MgH₂ and Nb₂O₅ and proceeded with increasing temperature. Here, it should be noticed that Mg phase appeared and grew up between MgH₂ and catalyst, indicating that MgH₂ phase did not touch the catalyst any longer. In that case, it should be considered that how the catalyst does work. In general, surface reaction is regarded as the rate determining step of the decomposition of MgH₂. On the surface, hydrogen molecules form with hydrogen atoms. The catalyst should rescue the activation energy of the surface reaction. So, it can be recognized that hydrogen molecules emitted at the interface. As a result, it can be suggested that hydrogen atoms diffuse from MgH₂ phase to the interface through Mg phase, as shown in Fig. 4. With respect to state of hydrogen atoms, initially hydrogen is as atoms in



This a successively observed the growth of Mg phase started at the subject to the FIG 4. Schematic of dehydrogenation process of MgH2 worldaded to IP:

hydride, next hydrogen atoms randomly diffuse in interstitial sites, and finally hydrogen atoms are combined to be hydrogen molecule at the interface between Mg and catalyst.

In conclusion, it was confirmed that the dehydrogenation of MgH₂ catalyzed with 1 mol % Nb₂O₅ started at 150 °C, and then nanosize Mg was formed by SADP. In the case of MgH₂ catalyzed with 10 mol % Nb₂O₅, it was indicated that the dehydrogenation of MgH₂ started at interface between Nb₂O₅ and MgH₂. And it can be assumed that hydrogen probably diffuse from MgH_2 to surface of Nb_2O_5 through Mg phase. The real catalyst, which might exist on the interface of Nb_2O_5 and MgH_2 could not be identified either. Hanada *et al.*¹¹ reported the catalyst of Nb–O binary oxides in MgH₂ was characterized to be NbO by x-ray absorption fine structure (XAFS). NbO was generated by ballmilling MgH₂ with Nb₂O₅. On the other hand, Porcu *et al.*¹² observed Nb₂O₅, Nb₂O, and MgNb₂O_{3.67} by TEM. Still several candidates can be considered for the most effective catalyst. Near future, we plan to observe the interface between MgH₂ and Nb₂O₅ by using scanning transmission electron microscope electron energy-loss spectroscopy (STEM-EELS), which can be a proper method to determine the real catalyst at the interface.

This work has been partially supported by NEDO under "Advanced Fundamental Research Project on Hydrogen Storage Materials."

- ¹J. Prigent and M. Gupta, J. Alloys Compd. 446-447, 90 (2007).
- ²X. L. Wang, J. P. Tu, P. L. Zhang, X. B. Zhang, C. P. Chen, and X. B. Zha, Int. J. Hydrogen Energy **32**, 3406 (2007).
- ³L. Schlapbach, D. Shaltiel, and P. Oelhafen, Mater. Res. Bull. **14**, 1235 (1979).
- ⁴G. Barkhordarian, T. Klassen, and R. Bormann, Scr. Mater. **49**, 213 (2003).
- ⁵G. Barkhordarian, T. Klassen, and R. Bormann, J. Alloys Compd. **364**, 242 (2004).
- ⁶G. Barkhordarian, T. Klassen, and R. Bormann, J. Alloys Compd. **407**, 249 (2006).
- ⁷N. Hanada, T. Ichikawa, and H. Fujii, J. Alloys Compd. **404–406**, 716 (2005).
- ⁸N. Hanada, T. Ichikawa, S. Hino, and H. Fujii, J. Alloys Compd. **420**, 46 (2006).
- ⁹N. Hanada, T. Ichikawa, and H. Fujii, Physica B 383, 49 (2006).
- ¹⁰N. Hanada, E. Hirotoshi, T. Ichikawa, E. Akiba, and H. Fujii, J. Alloys Compd. **450**, 395 (2008).
- ¹¹N. Hanada, T. Ichikawa, S. Isobe, T. Nakagawa, K. Tokoyoda, T. Honma, H. Fujii, and Y. Kojima, J. Phys. Chem. C 113, 13450 (2009).
- ¹²M. Porcu, A. K. Petford-Long, and J. M. Sykes, J. Alloys Compd. **453**, 341 (2008).