Fabrication and Characterization of Magnesium Nanoparticle by Gas Evaporation Method*

S. Ogawa[†] and H. Niwa

*Department of Quantum Engineering, School of Engineering,
Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*

T. Nomoto

Aichi Industrial Technology Institute, Onda-cho 1-157-1, Kariya-city 448-0013, Japan

S. Yagi

*Department of Quantum Engineering, School of Engineering,
Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan.*

(Received 10 January 2010; Accepted 18 March 2010; Published 15 May 2010)

We have fabricated the Mg nanoparticles by the gas evaporation method. The AFM observation shows Mg nanoparticles fabricated under the several gas pressures of He have the average diameter of 3.6 nm to 8.0 nm. We have studied the influence of the atmospheric oxidation for the chemical state of the Mg nanoparticles by the Mg K-edge NEXAFS technique. The NEXAFS measurement shows that the chemical state of MgCO_3 exists on the most lateral surface of the Mg nanoparticles and the degree of atmospheric oxidation depends on the size of Mg nanoparticles. [DOI: 10.1380/ejsnt.2010.246]

Keywords: Mg nanoparticle; Gas evaporation method; Atmospheric oxidation; AFM; NEXAFS

I. INTRODUCTION

The main energy resources are fossil fuel such as the oil, and the usage increases year by year. However, the environmental burden by using of large quantity of fossil fuel becomes very serious problem. Therefore, sustainable energy resources are required. The hydrogen is paid attention as the clean energy resources because the hydrogen generates only water when it reacts with the oxygen [1]. For use of the hydrogen as the fuel, we need to establish its effective storage technique.

Hydrogen storage material, which stores the hydrogen inside and releases it by heating, is required lightweight and inexpensive material compared with the hydrogen gas chamber [2]. The alloys based on Mg are more lightweight and inexpensive materials than other materials, and Mg possesses of 7.6 wt% storage for hydrogen [3]. Mg absorbs and desorbs hydrogen at high temperature range of 623-673 K [3], but MgNi alloy film coated with Pd can absorb and desorb hydrogen at room temperature and under atmospheric pressure [4].

Our idea to increase the hydrogen storage capacity of this film is increase of the surface area for reaction with hydrogen, in other words, fabrication of the film consists of nanoparticles. It is difficult to fabricate alloy nanoparticles because of difference of melting point of each component elements. Therefore, firstly we try to fabricate single component nanoparticles of Pd, Ni and Mg. After that, we try to fabricate the alloy nanoparticles by means of mixing three kinds of single nanoparticles. We have

already fabricated Pd and Ni nanoparticles [5]. In this study we have tried to fabricate Mg nanoparticles.

We pay attention to size dependence of hydrogen storage capacity of Mg nanoparticles. In the hydrogen storage of Mg, magnesium hydride (MgH_2) forms on the Mg surface firstly, and magnesium hydride layer prevents hydrogen atoms from penetrating to materials. Because the small nanoparticles have a larger specific surface area than the large ones, it is expected that the small Mg nanoparticles have high hydrogen storage capacity per its volume. For this reason, it is necessary to control the size of Mg nanoparticles for the fabrication of small Mg nanoparticles (about 1 or 2 nm) and to compare with the small Mg nanoparticles and large ones about hydrogen storage capacity.

It is known that Mg loses hydrogen storage ability by the atmospheric oxidation [3]. Mg surface is oxidized easily by exposure to atmosphere, and MgO layer produced by atmospheric oxidation prevents hydrogen molecules from penetrating into the material. By a long time exposure to atmosphere for about 20 days, magnesium carbonates are formed on the Mg lateral surface, and oxides and hydroxides are produced under the magnesium carbonates layer [6]. In the case of the highly humid air, hydroxy carbonates ($\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$) are formed [7].

In this study, we have fabricated the Mg nanoparticles and investigated the chemical state of Mg nanoparticles surface as a first step. The size of Mg nanoparticles is estimated by atomic force microscopy (AFM) observation and surface chemical state is studied by near-edge X-ray absorption fine structure (NEXAFS) measurement.

II. EXPERIMENTAL

The Mg nanoparticles were fabricated by the gas evaporation method [5]. Mg was evaporated at several kPa

*This paper was presented at 7th International Symposium on Atomic Level Characterizations for New Materials and Devices, The Westin Maui Resort & Spa, Hawaii, U.S.A., 6-11 December, 2009.

[†]Corresponding author: ogawa.satoshi@g.mbox.nagoya-u.ac.jp

FIG. 1: AFM images and size distributions of Mg nanoparticles deposited on Si wafer.

of He gas. Mg atoms are cooled down by He atoms and form nanoparticles by aggregation each other. The Mg nanoparticles were deposited on the Si substrate and the amount was controlled by the deposition time. Mg thin film (100 nm thickness) on Ni was fabricated by magnetron sputtering as the standard sample of Mg bulk.

The AFM observations were carried out under atmospheric condition by using Nanoscope IIIa (Veeco) by tapping mode. The Mg K-edge NEXAFS measurements were done at BL-10 of the SR center in Ritsumeikan University by total electron yield (TEY) method with sample drain current and fluorescence X-ray yield (FY) method with silicon drift detector. All NEXAFS spectra were obtained under high vacuum condition.

III. RESULTS AND DISCUSSION

A. AFM images

Figures 1(a), (b), and (c) show the AFM images of the Mg nanoparticles on Si substrate fabricated at 3, 5 and 10 kPa of He, respectively. Since the height value of the AFM analysis has a good resolution in comparison with the horizontal one, the diameter of nanoparticles is evaluated by the height value. Judging from the results of AFM observations, it is found that the Mg nanoparticles fabricated at 3, 5 and 10 kPa have the average diameter of 3.6, 8.0 and 5.0 nm, respectively. Yagi *et al.* have reported that Pd nanoparticles fabricated by the gas evaporation method have the diameter proportional to He gas pressure [5]. However, such tendency is not seen for the Mg nanoparticles in this study.

The melting point of Mg (923 K) is much lower than

FIG. 2: The relation between partial pressure of He and average diameter of Mg nanoparticles.

that of Pd (1828 K). Moreover, the vapor pressure of Mg at melting point is much higher than that of Pd. Both the low melting point and the high vapor pressure increase the evaporation rate of Mg source, and it causes much aggregation of Mg atoms. It is thought that the control of the size of Mg nanoparticles is difficult because the high evaporation rate of Mg is much more significant factor than the He gas pressure in the form of Mg nanoparticles.

In addition, we evaporate Mg source by the resistive heating of the tungsten (W) basket, and the setting position of Mg source on W basket is slightly different a little at each fabrication of Mg nanoparticles. A little difference of the setting position of source influences the evaporation rate significantly. Thereby, shown in Fig. 2, the repeatability of the size of Mg nanoparticles which fabricated under each partial pressures of He is not obtained.

B. Mg K-edge NEXAFS

Figures 3(A) and (B) show the Mg K-edge NEXAFS spectra for the Mg nanoparticles oxidized in atmosphere for about 20 days. The spectra in (A) and (B) have been taken by FY and TEY methods, respectively. As a standard sample, we have measured Mg bulk, MgO and magnesium hydroxy carbonates ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$).

In the (A)-(a)1 spectrum for small amount of deposition the peak associated with the chemical state of MgCO_3 [8] can be seen clearly, but in the (A)-(a)2 spectrum for large amount of deposition the peak of MgCO_3 is not seen clearly and the peak of MgO is significant. In the (A)-(b) spectrum the peak associated with the chemical state of Mg bulk can be observed. Since the peak top has a flat shape, it seems that both MgO and MgCO_3 compounds exist.

In the (B)-(a)1 spectrum the peak of MgCO_3 is seen clearly and the shoulder structure of MgO is also observed. The peak intensity of (B)-(a)2 spectrum becomes small because the peak of MgO is weakened by self absorption effect in fluorescence x-ray absorption. The shape of the (B)-(b) spectrum is almost similar with the (A)-(b) spectrum, but intensity of the peak of Mg bulk is higher than that of the (A)-(b) spectrum.

FIG. 3: Mg K-edge NEXAFS spectra for Mg nanoparticles measured by (A) TEY and (B) FY methods. All samples have been exposed to atmosphere for about 20 days.

These results mean that MgO and MgCO₃ exist on the surface of the Mg nanoparticles. Consider the deposition amount of Mg nanoparticles, it is thought that the adsorbate at lateral surface on Mg nanoparticles is dominantly MgCO₃. The Mg nanoparticles with average diameter of 5 nm are fully oxidized by atmosphere. On the other hand, metal Mg atoms exist inside of the Mg nanoparticle with average diameter of 8 nm.

Judging from the intensity of the shoulder structure associated with the chemical state of Mg bulk in NEXAFS spectra, following things can be said. The small nanoparticles have very large specific surface area, thereby the inside of the small nanoparticles are easily oxidized by atmosphere. With increase the size of nanoparticle, the specific surface area decreases and bulk component increases gradually. Therefore, it is thought that the large nanoparticles are difficult to progress atmospheric oxidation in comparison with the small nanoparticles.

We have speculated that the reaction time for the atmospheric oxidation of Mg nanoparticles becomes short because of the large specific surface area. However, it is revealed by the NEXAFS measurement that the atmospheric oxidation of Mg nanoparticles has not completed for about 20 days, and MgO and MgCO₃ have formed on the surface of Mg nanoparticles. We are going to clarify the variation of those products of the atmospheric oxidation for a long reaction time, for example several months, and the influence on hydrogen storage ability.

IV. CONCLUSION

We have fabricated the Mg nanoparticles by the gas evaporation method, but the size control has not been established. The chemical state of Mg nanoparticles has been characterized by Mg K-edge NEXAFS technique. It is found that the chemical state of MgCO₃ exists on the lateral surface of the Mg nanoparticles. By the exposure to atmosphere for 20 days, Mg nanoparticles with average diameter of 5 nm are fully oxidized, but metal Mg atoms exist inside of Mg nanoparticles with average diameter of 8 nm.

Acknowledgments

The authors are grateful for the financial supported of a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan (No. 19008872) and Knowledge Cluster II in Aichi/Nagoya area. This work was performed under the approval of Ritsumeikan University SR center Program Advisory Committee (No. S21-06). Especially NEXAFS measurements are supported by the nanotechnology network project of the Ministry Education, Culture, Sports, Science and Technology, JAPAN (MEXT).

[1] S. Dunn, *Int. J. Hydrogen Energy* **27**, 235 (2002).

[2] A. Züttel, *Materials Today* **6**, 24 (2003).

[3] A. Zaluska, L. Zaluski, and J. O. Strom-Olsen, *J. Alloys Compd.* **288**, 217 (1999).

- [4] K. Yoshimura, J. Surf. Finishing Soc. Jpn. **56**, 882 (2005).
- [5] S. Yagi, H. Sumida, K. Miura, T. Nmoto, K. Soda, G. Kutluk, H. Namatame, and M. Taniguchi, e-J. Surf. Sci. Nanotech. **4**, 258 (2006).
- [6] C. Fotea, J. Callaway, M R. Alexander, Surf. Interface Anal. **38**, 1363 (2006).
- [7] R. Lindstrom, L.-G. Johansson, G. E. Thompson, P. Skeldon, and J.-E. Svensson, Corr. Sci. **38**, 1363 (2006).
- [8] F. Farges, M.-P. Etcheverry, A. Haddi, P. Trocellier, E. Curti, and G. E. Brown Jr., XAFS 13 (2007).