Size Dependence of Air Oxidation for Mg Nanoparticle

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The size dependence of the air oxidation for Mg nanoparticles is studied by Mg K-edge NEXAFS and AFM techniques. In the case of the exposure to the air for 3 days, the degree of the air oxidation for Mg nanoparticles increases with reduction of the size of Mg nanoparticle. However, the opposite size dependence is observed in the case of the exposure to the air for 25 days, i.e. the air oxidation reaction for the smaller Mg nanoparticles is more inhibited in the case of long term exposure to the air. This size dependence is attributed to the occupation of the free spaces between Mg nanoparticles, which protects against the incursion of the air component molecules into the multilayer of Mg nanoparticles. [DOI: 10.1380/ejssnt.2011.315]

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I. INTRODUCTION

Hydrogen energy system is expected as the alternative energy system to the current fossil fuel system because hydrogen is efficient and clean energy source. It is important to establish the hydrogen storage technique for use of hydrogen energy system. Mg is attractive material for hydrogen storage application because of its high hydrogen storage capacity of 7.6 wt% [1]. The more favorable features of Mg for the hydrogen storage are inexpensiveness and lightness compared with other materials. The problem for practical use of Mg is that hydrogenation and dehydrogenation of Mg is very slow reaction (an order of a few hours) and occurs only at high temperature region (more than 350°C) [1]. The reaction temperature decreases by addition of Ni into Mg. The hydrogenation and dehydrogenation of the Mg2Ni alloy occur around 250°C due to the catalytic effect of Ni [2]. Nevertheless, further decrease of reaction temperature and time are required for the practical use of Mg material for the hydrogen storage application. Yoshimura et al. has reported that Mg-Ni alloy film capped with Pd, which is the hydrogen dissociation catalyst, can absorb/desorb the hydrogen at room temperature under atmospheric pressure within several tens of seconds [3]. Despite this ideal property as hydrogen storage material, the volume expansion of Mg-Ni alloy during hydrogenation causes the crack at the Pd cap layer and the incursion of the air into the film by the repeat of the hydrogenation and dehydrogenation. Consequently, Mg loses hydrogen storage ability by the air oxidation [4]. It is required to relax the volume expansion during hydrogenation for the practical use of Pd/Mg-Ni material. For the solution of this problem, we suggest
that the material is consisted of Pd, Ni and Mg nanoparticles (Pd nanoparticles layer/Ni and Mg nanoparticles multilayer). It is expected that the nano-sized free spaces between nanoparticles relax the volume expansion of the material during hydrogenation and improve the repeatability of the hydrogen storage.

The material consists of nanoparticles has very large specific surface area and many active surface sites per its volume in comparison with the bulk material. These features provide the improvement of the reaction activity with hydrogen and causes simultaneously easy oxidizability of the material. Especially, it is well known that Mg is easily oxidizes by the air [5, 6]. Therefore, we have investigated the air oxidation of Mg nanoparticles by the near edge X-ray absorption fine structure (NEXAFS) technique [7–9]. NEXAFS technique is suitable for determination of chemical species because NEXAFS spectrum is available as fingerprint of each chemical species. In our previous study, the process of the air oxidation reaction for Mg nanoparticle has been clarified. At initial stage of the air oxidation reaction, Mg nanoparticle reacts with oxygen (O$_2$) or water (H$_2$O) molecules in the air and magnesium oxide (MgO) forms. After that, magnesium hydroxide (Mg(OH)$_2$) is formed by the reaction of MgO with H$_2$O molecules. The Mg(OH)$_2$ reacts with carbon dioxide (CO$_2$) molecules in the air and the complex magnesium carbonates ($x$MgCO$_3$.Mg(OH)$_2$.yH$_2$O) forms. Finally, basic magnesium carbonate (4MgCO$_3$.Mg(OH)$_2$.4H$_2$O: BMC) is formed as the product of the reaction of the complex magnesium carbonate with CO$_2$ and H$_2$O molecules in the air. In the case of the multilayer of Mg nanoparticles, the air component molecules penetrate through the nano-sized free spaces between Mg nanoparticles and BMC forms evenly in the multilayer of Mg nanoparticles [9].

The increase of the specific surface area and the number of active surface sites occur with the decrease of the size of nanoparticle. We have reported briefly the size dependence of the degree of the air oxidation reaction for Mg nanoparticles [7, 8]. The smaller Mg nanoparticles are more rapidly oxidized by the exposure to the air due to the increase of the reaction activity [7]. However, in the case of the longer exposure to the air, the size dependence opposite to the shorter exposure has observed, i.e. the air oxidation of smaller Mg nanoparticles less progresses than that of larger ones [8]. In this work, we have studied the details of the size dependence of the air oxidation for Mg nanoparticles by NEXAFS, atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) techniques. AFM and XPS techniques were used for observation of surface morphology and characterization of surface chemical state, respectively.

II. EXPERIMENTAL

Mg nanoparticles were fabricated by the gas evaporation method using He gas [7, 10]. The rod-shaped Mg (purity: 99.98%) was used as evaporation source. The Mg source evaporates in the He gas (purity: 99.99995%) atmosphere and Mg atoms condense into the Mg nanoparticle. The size of Mg nanoparticles is varied by He gas pressure in the fabrication chamber (6-14 kPa). The Mg nanoparticles were deposited on Si single-crystal substrate and Ni polycrystalline substrate. The Si substrate is suitable for the estimation of the size of Mg nanoparticle by the AFM observation due to its good flatness. The Ni substrate was used as the conventional substrate for NEXAFS and XPS measurements [11–13]. The deposition amount of Mg nanoparticles was controlled by deposition time. The amount of Mg nanoparticles on Si and Ni substrates were less than 1 ML and multilayer (nominal thickness estimated by AFM: 97.6±45.4 nm), respectively. The fabrication chamber is connected to XPS chamber and in-situ XPS measurement is possible after evacuation of He gas in the fabrication chamber to ~5×10$^{-6}$ Pa and transfer of sample to XPS chamber. The Mg nanoparticles deposited on Ni substrate were exposed to the air under the laboratory environment (35–45% RH) at room temperature (around 20°C) for 3 or 25 days prior to NEXAFS measurements.

The diameter of Mg nanoparticles was estimated by AFM observation. Figure 1 shows AFM image of the typical monodispersed Mg nanoparticles deposited on Si substrate. The AFM image in Fig. 1 was obtained with tapping mode under the atmospheric condition. The diameter of Mg nanoparticles has been estimated by the height value of AFM observation because of high resolution in vertical direction of AFM observation compared with horizontal one [10]. The size distribution of Mg nanoparticles is shown as inset in Fig. 1. It is estimated by the AFM observation that the average diameter of Mg nanoparticles in Fig. 1 is 1.6 nm.

In order to identify chemical state of the Mg nanoparticles exposed to the air, Mg K-edge NEXAFS measurements using synchrotron radiation were carried out for Mg nanoparticles deposited on Ni substrate at BL-10 of the SR center in Ritsumeikan University [14]. A Golovchenko-type double-crystal monochromator with beryl(10-10) crystal was used for the selection of incident X-ray energy around the energy region of Mg K-edge absorption. NEXAFS spectra were obtained simultaneously by both fluorescence X-ray yield (FY) method with sil-
con drift detector and total electron yield (TEY) method with sample drain current under high vacuum condition ($7 \times 10^{-6}$ Pa). The sampling depth is different between FY and TEY methods because of the difference of mean free pass inside of solid between photon and electron. The sampling depth of FY and TEY methods are several hundreds and <50 nm, respectively [15, 16]. The incident X-ray energy was calibrated with the first peak of the NEXAFS spectrum for MgO powder (purity: 99%) at 1309.5 eV.

XPS is high surface sensitive technique (sampling depth: <10 nm) because only primary electrons contribute to formation of XPS peak. In this study, the surface chemical analysis of the most lateral Mg nanoparticles exposed to the air was undertaken by XPS technique. XPS measurements were carried out using monochromated Mg Kα X-ray (1253.6 eV) source and a hemispherical electron energy analyzer (PHOIBOS 100, SPECS) with channeltron detectors (5 ch). The base pressure of XPS analysis chamber was $2 \times 10^{-7}$ Pa. All XPS spectra were obtained in the fixed analyzer mode with pass energy of 10 eV. The binding energy scale of the XPS measurements was calibrated with Mo 3d$_5$/2 photoelectron peak of the sample holder at 228.0 eV.

III. RESULTS AND DISCUSSION

A. Mg K-edge NEXAFS analysis of Mg nanoparticles exposed to the air

NEXAFS analysis enables to determine the chemical state of Mg nanoparticles over a range of sampling depth. Figure 2 shows Mg K-edge NEXAFS spectra for Mg nanoparticles exposed to the air. The average diameters of each Mg nanoparticle samples are 1.4, 8.2, 10.6 nm, respectively. All samples were removed from the fabrication chamber at once and exposed to the air for 3 days. Mg K-edge NEXAFS spectra for metallic Mg (purity: 99.98%) are also shown as a standard spectrum. Figures 2(A) and (B) show the NEXAFS spectra obtained by FY and TEY methods, respectively. All spectra in Fig. 2 were normalized with respect to height of the edge jump. The insets of (A) and (B) show the magnification of the shoulder structures of the spectra for Mg nanoparticles.

FIG. 2: Mg K-edge NEXAFS spectra for Mg nanoparticles exposed to the air for 3 days. Mg K-edge NEXAFS spectra for metallic Mg are also shown as a standard spectrum. The NEXAFS spectra have been obtained by (A) FY and (B) TEY methods, respectively. All spectra are normalized with respect to height of the edge jump. The insets of (A) and (B) show the magnification of the shoulder structures of the spectra for Mg nanoparticles.

FIG. 3: Mg K-edge NEXAFS spectra for Mg nanoparticles exposed to air for 25 days. Mg K-edge NEXAFS spectrum for BMC is also shown as a standard spectrum.
spectra for metallic Mg, it is apparent that the shoulder structure around 1304 eV in the spectra for the Mg nanoparticles is associated with the component of metallic Mg in the Mg nanoparticles. The height of the shoulder structure decreases with the exposure of Mg nanoparticles to the air. Therefore, the height of the shoulder structure corresponds to the residual amount of metallic Mg in the Mg nanoparticles [9]. A comparison of the height of the shoulder structure between the spectra in Fig. 2 indicates size dependence of the degree of the air oxidation for Mg nanoparticles.

The dashed lines in Fig. 2 show the energy position of the shoulder structure associated with metallic Mg and the inset in Figs. 2(A) and (B) show the magnification of the spectra for Mg nanoparticles in the energy range of 1300-1310 eV. It is apparent from the inset in Figs. 2(A) and (B) that the height of the shoulder structure for the smaller Mg nanoparticles is lower than that for larger ones, i.e. the smaller Mg nanoparticles is oxidized more rapidly. This size dependence for the air oxidation is attributed to increase of specific surface area with reduction of the size of the Mg nanoparticles. The reduction of the size of nanoparticle increases the ratio of number of surface atoms to that of total atoms and the amount of reactive surface sites per its volume. Nanoparticle with the size of less than 3 nm shows remarkably these effects [17]. The size dependence of the air oxidation for Mg nanoparticle in Fig. 2 is originated in the activation of Mg nanoparticle with reduction of its size.

However, the opposite size dependence in Fig. 2 is observed for longer exposure of Mg nanoparticle to the air. Figure 3 shows Mg K-edge NEXAFS spectra for Mg nanoparticles exposed to the air for 25 days. The average diameters of each Mg nanoparticle samples are 1.6 and 3.8 nm, respectively. Mg K-edge NEXAFS spectrum for BMC (reagent grade) is also shown as a standard spectrum. All spectra was obtained by TEY method and normalized with respect to height of the edge jump. The shoulder structure around 1304 eV in the NEXAFS spectrum for the Mg nanoparticles with average diameter of 1.6 nm indicates the existence of residual metallic Mg inside of the Mg nanoparticles. On the contrary, in spite of the larger average diameter, the shoulder structure is not seen in the NEXAFS spectrum for the Mg nanoparticles with average diameter of 3.8 nm, namely these Mg nanoparticles are fully oxidized by the air. These tendencies are opposite to the results in Fig. 2 and can not be explained by the size dependence of specific surface area. Furthermore, it is apparent from the NEXAFS peaks in the energy range of 1307-1320 eV that the formation of BMC in the Mg nanoparticles with average diameter of 3.8 nm progresses more rapidly than that of 1.6 nm. Of course, the NEXAFS spectra obtained by FY method shows same size dependence with Fig. 3, not shown here. The both NEXAFS spectra for Mg nanoparticles with average diameter of 1.6 and 3.8 nm have shoulder structures around 1304 eV and the height of the shoulder structure increases with reduction of the size of Mg nanoparticle. These results imply that there is difference in the size dependence of the air oxidation of Mg nanoparticle between short term and long term exposure to the air.

We have considered several factors that are possible to cause the size dependence of the air oxidation for Mg nanoparticles in Fig. 3. An oxidation of metal is described generally by the Mott-Cabrera mechanism, the oxide layer grows by the field assisted transportation of ion and tun-
FIG. 6: AFM images of the Mg nanoparticles exposed to the air for 3 days. The average diameters of the Mg nanoparticles in left hand side and right hand side are 1.4 and 10.6 nm, respectively. The line profiles of AFM images are also shown below the each AFM images.

FIG. 7: The XPS peak area ratio of $[C_{1s}]$ and $[O_{1s}]$ to $[Mg_{2p}]$. The horizontal axis represents the time of exposure to the air.

neling electron across the oxide layer [16]. In the case of metal nanoparticle, it is reported by Sako et al. that the increase of transfer energy of charge occurs with the reduction of the size of nanoparticle and the growth of oxide layer is suppressed [17]. Although the oxide layer becomes thinner with decrease of the size of nanoparticle, the mass ratio of surface oxide to total mass increases simultaneously. Thereby, the increase of transfer energy of charge is not the factor for the size dependence of the air oxidation in Fig. 3. The inhibition of BMC formation in the smaller Mg nanoparticles in Fig. 3 indicates that the factor for the size dependence in Fig. 3 is the effect which inhibits the BMC formation reaction, namely preventing air component molecules ($O_2$, $H_2O$ or $CO_2$) from incursion into the multi layer of Mg nanoparticles. One of the effects to prevent the incursion of the air component molecules is volume expansion of Mg nanoparticles by the air oxidation. The molar volume of magnesium carbonate (e.g. $MgCO_3.3H_2O$) is five times larger than that of metallic Mg [18]. If the volume expansion is the factor of the size dependence in Fig. 3, the same dependence is observed in the case of the short exposure to humid air of Mg nanoparticles because humidity in the air accelerates the formation of BMC [9]. Figure 4 shows the Mg K-edge NEXAFS spectra obtained by FY method for Mg nanoparticles exposed to the humid air (more than 90% RH) for 3 days. The same size dependence with Fig. 3 is not seen in Fig. 4. The NEXAFS spectra obtained by TEY method also show that carbonation reaction progresses more rapidly at the smaller Mg nanoparticles, not shown here. As these results, it is thought that the volume expansion of Mg nanoparticles during the air oxidation is not the factor of the size dependence in Fig. 3.

B. AFM observation of the morphology of lateral Mg nanoparticles

The size dependence of the air oxidation for Mg nanoparticles in Fig. 3 is observed in only the case of long term exposure to the air. As the factor of this size dependence, the effect to prevent the incursion of the air component molecules can be considered. In order to clarify this effect, we have investigated the time variation of morphology for Mg nanoparticles during the exposure to the air. Figure 5 shows AFM images of lateral surface of the Mg nanoparticles exposed to the air. Figures 5(a) and (b) show AFM images for the Mg nanoparticles exposed to the air for 3 and 25 days, respectively. Mg nanoparticles in Fig. 5(a) have uniform sizes and shapes. On the contrary, larger round objects with random sizes are seen in Fig. 5(b). These results indicate that reaction products with the air are formed by the long term exposure to the air on the lateral surface of the Mg nanoparticles. It is apparent by the AFM observation in Fig. 5 that the reaction products are very large compared with the Mg nanoparticles. It is speculated that the reaction products occupy free spaces between Mg nanoparticles by the long term exposure to the air and prevent from the incursion of molecules in the air.
If the formation of the reaction products causes the size dependence of the air oxidation for Mg nanoparticles in Fig. 3, the same size dependence must be observed in the formation of the reaction products. Figure 6 shows the AFM images of Mg nanoparticles with the average diameters of (i) 1.4 and (ii) 10.6 nm. Both Mg nanoparticle samples have been exposed to the air for 3 days. The line profiles of the AFM images are also shown in below the each AFM images in Fig. 6. In spite of the smaller average diameter of 1.4 nm, the line profile at Fig. 6(i) shows the rougher lateral surface of Mg nanoparticles compared with Fig. 6(ii). This can be attributed to the deference of surface reactivity depending on the size of Mg nanoparticle. The smaller Mg nanoparticles have the more reactive surface. Therefore, the reaction products with the air are formed rapidly on the lateral surface of small Mg nanoparticles and occupy the free spaces between Mg nanoparticles.

C. Surface chemical analysis of lateral Mg nanoparticles by XPS technique

The surface chemical analysis by XPS indicates the chemical composition of the reaction products on the Mg nanoparticles. Especially, we focus on the time variation of the surface chemical state of Mg nanoparticles by the exposure to the air from 1 hour up to 25 days. Figure 7 shows the ratio of XPS peak area for C 1s and O 1s core-level peaks to Mg 2p core-level peak versus the time of exposure to the air. The numerical data for [C 1s]/[Mg 2p] and [O 1s]/[Mg 2p] are drawn under consideration of the atomic sensitivity for XPS [19]. Figure 7 shows clearly that increase of the [C 1s]/[Mg 2p] and [O 1s]/[Mg 2p] ratio with the time of exposure to the air. Any other photoelectron peak area has not shown remarkable increase over the time of exposure to the air. As these results, it is apparent that the reaction products in Fig. 5(b) are composed of carbon and oxygen atoms, namely they are organic compounds.

High resolution XPS analysis provides details of chemical state of the reaction products. Figures 8, 9 and 10 show the Mg 2p, C 1s and O 1s core-level photoelectron spectra for the Mg nanoparticles exposed to the air for 25 days, respectively. The spectra in Figs. 8, 9 and 10 are deconvoluted into 3 or 5 components. Figure 8 shows that most of the metallic Mg has been oxidized by the air and two XPS components are present at high binding energy side of the peak of metallic Mg (49.7 eV). The XPS peak at 51.0 eV has been observed in the in-situ measurement for Mg nanoparticles. We assigned this component to the chemical state of MgO and Mg(OH)\(_2\) (Mg\(^{2+}\)) and this assignment is consistent with O 1s core spectrum (531.3 eV for MgO and 533.4 eV for Mg(OH)\(_2\)) [29–31]. The XPS peak at 52.2 eV has been seen just after the exposure to the air and has grown during the exposure. Considering NEXAFS results indicates that the XPS peak at 52.2 eV is attributed to complex magnesium carbonates (\(x\)MgCO\(_3\), Mg(OH)\(_2\), yH\(_2\)O). Figures 9 and 10 show the existence of various organic compounds on the lateral surface of Mg nanoparticles, for example ester, ether, carboxylate and carbonate. Both main XPS components in the Figs. 9 and 10 include ether (C–O–C). These results imply that the reaction products consist mainly of the
IV. CONCLUSION

We have investigated the size dependence of the air oxidation for Mg nanoparticles by Mg K-edge NEXAFS measurements. In the case of short term exposure (3 days) to the air, the degree of the air oxidation for Mg nanoparticles increases with reduction of the size of Mg nanoparticle due to the improvement of the specific surface area. On the contrary, in the case of long term exposure (25 days), the opposite size dependence is observed, i.e. the air oxidation reaction for the smaller Mg nanoparticles is more inhibited. The AFM observations and XPS measurements indicate that organic compounds form on the lateral surfaces of Mg nanoparticles. The organic compounds grow gradually over the exposure to the air and occupy the free spaces between Mg nanoparticles, which prevent air component molecules from incursion into the multilayer of Mg nanoparticles. It is thought that the formation of the organic compounds occurs more easily on the smaller Mg nanoparticles because of high surface reactivity.

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