Paper

Influence of CO_2 and H_2O on Air Oxidation of Mg Nanoparticles Studied by NEXAFS

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Influence of CO_2 and H_2O on the air oxidation reaction of Mg nanoparticles has been investigated by Mg K-edge NEXAFS technique. The water vapor in the air causes rapid progression on the air oxidation reaction of the Mg nanoparticles. The basic magnesium carbonate ($4(MgCO_3).Mg(OH_2).4(H_2O)$: BMC) is formed by the long term exposure to air. The NEXAFS analysis shows an existence of several intermediates of the BMC formation reaction.

1. Introduction

Magnesium (Mg) is attractive material for hydrogen storage application because Mg is inexpensive and lightweight and possesses high hydrogen storage capacity (7.6 wt%) [1]. The problem for practical use of Mg is that hydrogenation/dehydrogenation reaction of Mg is very slow (an order of a few hours) and occurs only at high temperature (more than 600 K) [1]. On the other hand, the hydrogenation/ dehydrogenation of Mg-Ni alloy occurs at lower temperature by the catalytic effect of Ni compared with pure Mg [2]. Nevertheless, further decrease of reaction temperature and time are necessary for practical application. Yoshimura 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 a few seconds [3]. However, the volume expansion of Mg-Ni alloy material during hydrogenation causes the cracking at the interface between Pd and Mg-Ni alloy and the incursion of air into the alloy film. Consequently, Mg loses hydrogen storage ability by the air oxidation. We suggest inducing nano-sized free spaces for reducing the effect of the volume expansion during the hydrogenation, in other words the fabrication of the material consists of nanoparticles. It is expected that the free spaces between nanoparticles relax the volume expansion of material during hydrogenation and improve the hydrogen storage property.

We have fabricated Pd, Ni and Mg nanoparticles by the gas evaporation method already and have been investigating the air oxidation mechanism of Mg nanoparticle for understanding its deterioration reaction [4, 5]. In our previous study, we have shown that magnesium oxide (MgO) and basic magnesium carbonate (BMC) form in the air oxidation of the Mg nanoparticles [5]. Moreover, the BMC forms dominantly by the long term exposure to air [6]. It is speculated that reactive species of the air oxidation is not only oxygen but also carbon dioxide (CO_2) and water vapor (H_2O) in the air. However, it is not clarified which reactive species is dominant factor in the air oxidation reaction of Mg nanoparticle.

In this study, we have investigated mechanism of air oxidation of the Mg nanoparticles by near-edge X-ray absorption fine structure (NEXAFS) measurement. In particular, we discuss the influences of CO_2 and H_2O of air components.

2. Experimental

Mg nanoparticles were fabricated by the gas evaporation method using He gas [5]. Mg nanoparticles were deposited on Si single-crystal substrate and Ni polycrystalline substrate. The deposition amount of Mg nanoparticles was controlled by deposition time. The amount of Mg nanoparticles on Si and Ni substrates were less

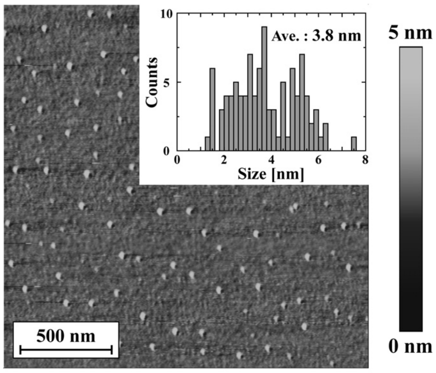

Fig. 1. AFM image and size distribution of the typical Mg nanoparticles deposited on Si substrate.

than 1 ML and multi-layer, respectively.

Atomic force microscopy (AFM) observation was carried out for estimation of the diameter of Mg nanoparticles. Fig. 1 shows AFM image of the Mg nanoparticles deposited on Si substrate. 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 [4]. The size distribution of Mg nanoparticles is shown as inset in Fig. 1. It is found by the AFM observation that the average diameter of Mg nanoparticles in Fig. 1 is 3.8 ± 1.4 nm.

Mg nanoparticles deposited on Ni substrate were exposed to air, CO_2 (gas) or H_2O (vapor) at room temperature for investigation of influence of CO_2 and H_2O on the air oxidation reaction. The exposure to air was done in laboratory atmosphere. Relative humidity in laboratory was 35-45 %RH. The reaction vessel filled with CO_2 gas (more than 0.1 MPa) was used for the exposure of the Mg nanoparticles to CO_2 gas. The Mg nanoparticles were exposed to H_2O in plastic bag filled with water vapor. Relative humidity in the plastic bag was more than 90 %RH.

In order to identify chemical state of Mg nanoparticle samples, Mg K-edge NEXAFS measurements were carried out with Mg nanoparticles deposited on Ni substrate at BL-10 of the SR center in Ritsumeikan University [7]. NEXAFS spectra were obtained simultaneously by both fluorescence X-ray yield (FY) method with silicon drift detector and total electron yield (TEY) method with sample drain current under high vacuum condition. The FY or TEY method is sensitive for bulk or surface, respectively.

3. Results and discussion

Fig. 2 shows Mg K-edge NEXAFS spectra for Mg nanoparticle samples (average diameter : 3.8 ± 1.4 nm) exposed to air, CO_2 or water vapor (H_2O) for 25 days. The spectra of (A) and (B) in Fig. 2 have been obtained by FY and TEY methods, respectively. Mg K-edge NEXAFS spectra for metallic Mg, MgO powder, $Mg(OH)_2$ powder and BMC powder are also shown in Fig. 2 as standard NEXAFS spectra. All spectra have been normalized with height of the edge jump.

Influences of CO_2 and H_2O atmospheres to Mg

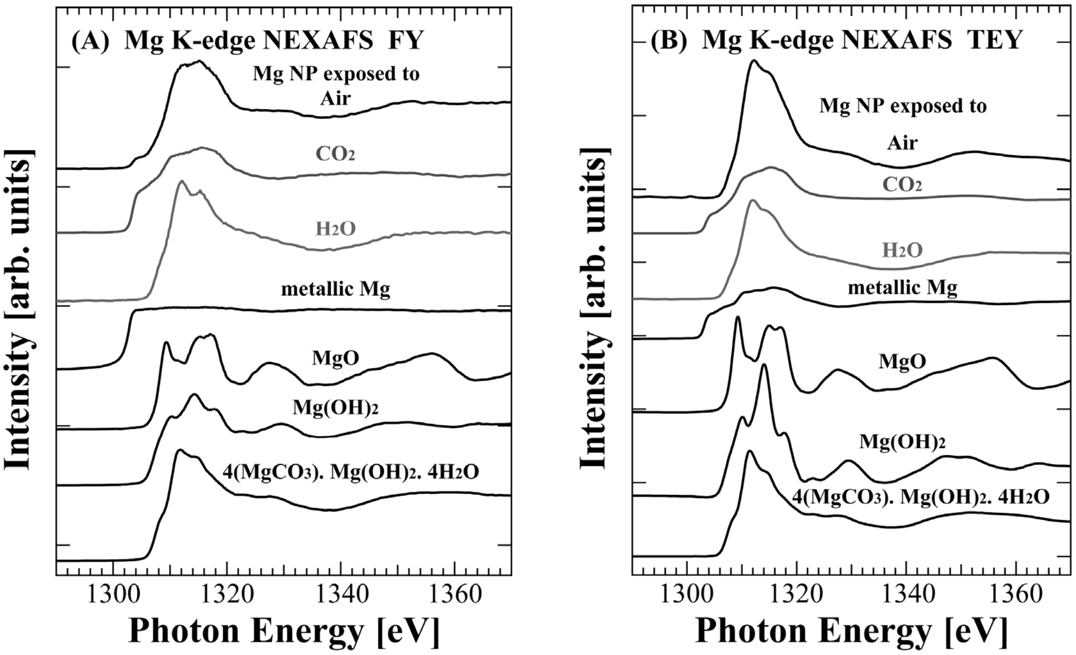

Fig. 2. Mg K-edge NEXAFS spectra for Mg nanoparticles exposed to air, CO_2 or water vapor (H_2O). The NEXAFS spectra have been obtained by (A) FY and (B) TEY methods. The peak heights of the spectra obtained by FY method are lower than those of the spectra obtained by TEY method because of a self absorption effect in fluorescence X-ray absorption.

nanoparticles are clearly reflected in the height of shoulder peak (1304 eV) associated with chemical state of metallic Mg in Fig. 2 (A). The shoulder peak is seen in the NEXAFS spectra for Mg nanoparticle samples exposed to air or CO_2 gas, and the height of shoulder peak for the sample exposed to CO_2 is higher than that for the sample exposed to air. These results mean that the metallic Mg exists in the samples exposed to air or CO_2 and much amount of metallic Mg exist in the sample exposed to CO_2. On the other hand, the shoulder peak at 1304 eV disappears in the spectrum for the sample exposed to water vapor. Judging from the shape of the spectrum, BMC forms dominantly at the sample exposed to water vapor.

The large difference between NEXAFS spectra obtained by FY and TEY methods in Fig. 2 can not be seen except the sample exposed to air. The NEXAFS spectrum for the sample exposed to air in Fig. 2 (B) shows that BMC is formed at the sample exposed to air. Considering the difference of sampling depth between FY and TEY methods, BMC is formed mainly at most top layer of Mg nanoparticles exposed to air.

From these results, it is apparent that increasing of water vapor in the air causes rapid formation of BMC at the Mg nanoparticles. Therefore, it is thought that $Mg(OH)_2$ is intermediate of the formation reaction of BMC in addition to MgO. At the initial stage of air oxidation, MgO forms immediately by the exposure to air. In the atmosphere containing water vapor, H_2O molecules adsorb and react with MgO or possibly metallic Mg and $Mg(OH)_2$ is formed consequently. Finally, formation of BMC occurs as a result of the reaction of $Mg(OH)_2$ with CO_2.

The peak structures at 1307-1320 eV correspond to products of the air oxidation, for example MgO, $Mg(OH)_2$ or BMC. In order to assign precise composition, the simulation of the NEXAFS spectra for the Mg nanoparticles (average diameter : 8.2 ± 2.0 nm) exposed to air for 3 and 25 days (dotted line) are shown in Fig. 3. The simulation of NEXAFS spectra has been attempted by superposition of the standard NEXAFS spectra for metallic Mg, MgO, $Mg(OH)_2$ and BMC.

However, it is very difficult to simulate completely the NEXAFS spectra. The peak structure around 1316 eV can not be simulated by superposition of the standard NEXAFS spectra. This result indicates the existence of other component in the NEXAFS spectra for the samples. Therefore, we have attempted the subtraction of the NEXAFS spectra to clarify the other component. The superposition spectra of the standard NEXAFS spectra are shown by solid line and the residual spectra as a result of subtraction are shown by dashed line in Fig. 3. The extended figures of residual spectra are also shown in Fig. 3.

Both the residual spectra for Mg nanoparticles exposed to air for 3 and 25 days show main peak at 1316 eV. It is reasonable to assign this peak to the chemical state of the complex magnesium carbonates ($x(MgCO_3).Mg(OH_2).y(H_2O)$) because the main peak of NEXAFS spectrum for simple magnesium carbonate ($MgCO_3$) lies around 1313 eV [8] and the compounds containing nitrogen are not detected in study by C. Fotea et al. for Mg film exposed to air [9]. The complex magnesium carbonates are stable or metastable in the air and usually exist as the minerals. For example BMC and $MgCO_3$ correspond to the hydromagnesite and magnesite, respectively. F. Farges et al. have measured various minerals containing magnesium carbonates by NEXAFS [10]. The shape of the NEXAFS spectra in this work for nesquehonite ($Mg(HCO_3)(OH).2(H_2O)$) and artinite ($MgCO_3.Mg(OH_2).3(H_2O)$) are similar to that of residual spectra in Fig. 3. As a

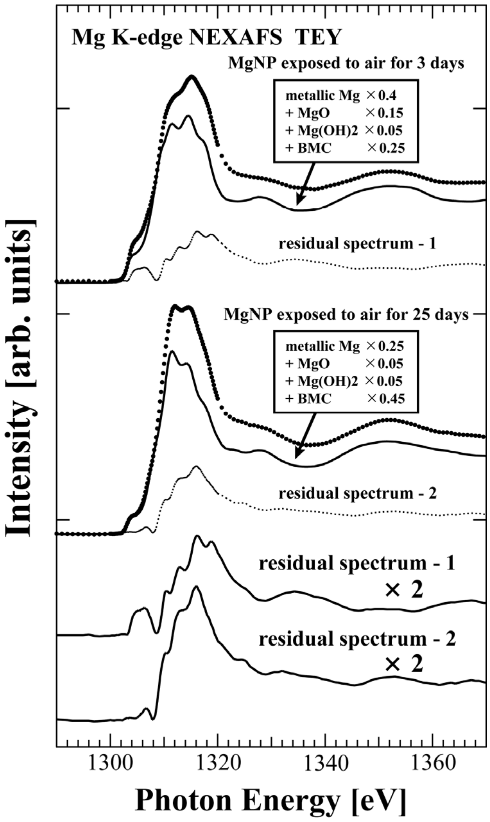

Fig. 3. Mg K-edge NEXAFS spectra obtained by TEY method with Mg nanoparticles exposed to air for 3 and 25 days. The superposition of the standard NEXAFS spectra and the residual spectra are also shown.

result, it is thought that complex magnesium carbonate exists as intermediate of BMC formation reaction.

For comparison of difference of the air oxidation reaction between nanoparticle and bulk material, Mg K-edge NEXAFS spectra for Mg thin film exposed to air for more than 1 year are shown in Fig. 4. This thin film was prepared by DC magnetron sputtering and its nominal thickness is about 100 nm. The FY spectrum in Fig. 4 shows that $Mg(OH)_2$ forms dominantly inside of the thin film and metallic Mg partly exists. The NEXAFS peaks at 1310 and 1318 eV in the TEY spectrum is unclear compared with the FY spectrum. The peak structures associated with magnesium carbonates appear around this energy region. Therefore, it is thought that carbonates exist on the surface of the Mg thin film.

In the oxidation of bulk Mg, MgO forms initially and the oxide layer grows [9]. H_2O molecules adsorb and $Mg(OH)_2$ forms in the presence of sufficient water vapor in the air. Furthermore, the formation of $Mg(OH)_2$ progresses toward depth direction [11]. Consequently, $Mg(OH)_2$ forms dominantly inside of Mg thin film. Magnesium carbonates are formed on the surface of bulk Mg by adsorption CO_2 or organic compounds because thick magnesium carbonates layer prevent farther growth of oxide layer [11]. However, in the case of Mg nanoparticles BMC is formed at a large part of the Mg nanoparticles [6]. This difference of air oxidation products between bulk material and nanoparticle represents the difference of specific surface area. Nanoparticle has large specific surface area compared with bulk. Therefore, BMC is formed evenly at the Mg nanoparticles. The BMC formation at the large part of Mg nanoparticles implies that CO_2 and H_2O molecules can penetrate through the nano-sized free spaces between Mg nanoparticles.

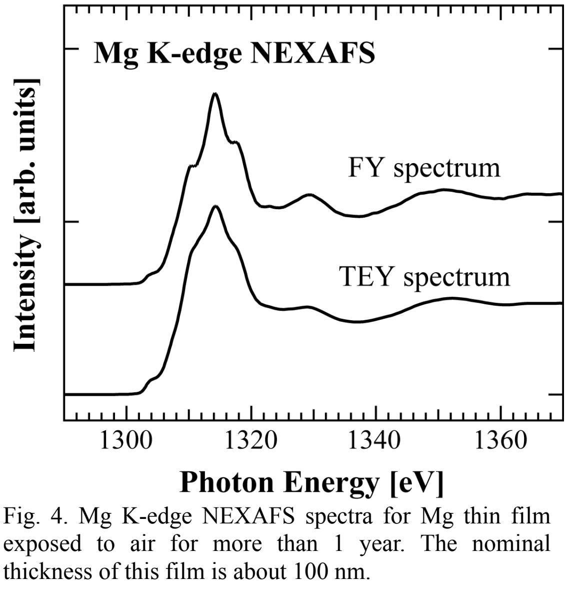

Fig. 4. Mg K-edge NEXAFS spectra for Mg thin film exposed to air for more than 1 year. The nominal thickness of this film is about 100 nm.

4. Conclusion

Influences of CO_2 and H_2O on the air oxidation reaction of Mg nanoparticles have been investigated by Mg K-edge NEXAFS technique. The water vapor is main factor of the air oxidation reaction. In the presence of water vapor in the air, $Mg(OH)_2$ forms at the Mg nanoparticles. Consequently, BMC is formed by CO_2 adsorption. It is thought that the complex magnesium carbonate exists as the intermediate of BMC formation reaction.

Acknowledgments

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