Correlation between Structure of Titanium Additives and Dehydrogenation Reaction of Magnesium Borohydride Studied by Continuous Observation of X-Ray Absorption Spectroscopy

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Local structure of Ti-based additives in Mg(BH₄)₂ was studied by X-ray absorption fine structure spectroscopy with conventional and dispersive mode in order to understand the correlation between the structure of the additives and dehydrogenation property of Mg(BH₄)₂. Simultaneous measurement of the dehydrogenation curve and the X-ray absorption spectroscopy by the dispersive optics revealed that a part of TiCl₃ additive in Mg(BH₄)₂ is immediately converted to Ti₂Mg₁₋ₓ(CH₃)ₓ(BH₄)₂⁺ after ball milling mixture and then promptly resolved to TiB₂ at 100–150 °C with the first dehydrogenation peak. TiO₂ additive is slowly converted to lower oxidation state in wide temperature range around the second dehydrogenation peak at 350 °C where the main dehydrogenation reaction of Mg(BH₄)₂ occurs. [doi:10.2320/matertrans.MA201018]

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1. Introduction

Development of advanced hydrogen storage materials with high hydrogen volumetric and gravimetric densities, moderate operation temperatures, and high dehydrogenation and rehydrogenation rates is highly required for onboard storage materials. Complex hydride is one of the candidates for the hydrogen storage materials because it contains many hydrogen atoms in one molecule.¹⁻³ Magnesium borohydride Mg(BH₄)₂, has a high hydrogen density of 14.9 mass% and 125 kg H₂/m³, has been regarded as one of the potential hydrogen storage materials.⁴⁻⁷ However, its high dehydrogenation temperature (>300 °C) highly restricted its potential applications. Recent study reported that Ti compounds largely lowered the dehydrogenation temperature of Mg(BH₄)₂: TiCl₃ and TiO₂ addition decreases the initial dehydrogenation temperature of Mg(BH₄)₂ by 170 and 50 °C, respectively.⁴⁻⁷ These results motivate us to clarify the effect of the addition of TiCl₃ and TiO₂ on the dehydrogenation reaction of Mg(BH₄)₂.

X-ray absorption fine structure (XAFS) technique is one of the powerful tools for the element selective determination of local structure. Observation of static XAFS spectra of the additives below and above the dehydrogenation temperature can clarify the contribution of the additives to the dehydrogenation reaction. However, because the dehydrogenation reaction itself is the time-dependent effect, the continuous observation of the XAFS spectra is desired for the exact determination of the correlation between the local structure of additive and the dehydrogenation reaction. Simultaneous observation of the local structure and the dehydrogenation reaction is suitable for understanding the actual active phase of additives contributing to the dehydrogenation reaction.

In this study, the local structure of Ti-based additives in Mg(BH₄)₂ was studied from the viewpoint of dynamics. Dispersive optics for XAFS observation is an attractive tool because it does not contain the mechanical motion module during observation of the X-ray absorption spectroscopy, which enables us to get the stable and fast XAFS spectra.⁸⁻⁹ Simultaneous observation of XAFS spectra by the dispersive optics and dehydrogenation curves by quadruple mass spectroscopy (QMS) was operated. The effectiveness of a simultaneous measurement of a chemical reaction by several detection systems has been established in the study of the catalysis.¹⁰ Complete time axes for the XAFS spectra and the dehydrogenation curves make the experiment reliable and clarify the correlation between the local structure of the Ti additives and the dehydrogenation properties of the storage materials of Mg(BH₄)₂.

2. Experiments

Mg(BH₄)₂ was synthesized from MgCl₂ (95%, Aldrich) and NaBH₄ (99.99%, Aldrich) in dehydrated diethyl ether (Cica-Reagent, Kanto Chemical), as described in the previous report.¹¹ TiCl₃ (95%, Toho Titanium Co., Ltd.) and TiO₂ (mixture of anatase and rutile) were used for an additive without purification. Samples of Mg(BH₄)₂ + xTiCl₃ with x = 0.02 and 0.10 mol, and Mg(BH₄)₂ + 0.02 mol TiO₂ were prepared by planetary ball milling (Fritsch P-7) with 20 steel balls (7 mm in diameter) in a hardened steel vial (30 cm³ in volume) under 0.1 MPa Ar for 5 h. The handling of the samples was always performed in a glove box filled with purified Ar/He gas (dew point below −90 °C; oxygen concentration lower than 1 ppm) to avoid (hydro-)oxidation.

The XAFS measurements were performed at the bending magnet beamline BL14B1 of SPring-8. This beamline has the apparatus of both the conventional and dispersive XAFS observation systems.¹¹,¹² The synchrotron beam current was kept to 100 mA by top-up mode at 8 GeV storage ring.
A Si(111) double-crystal monochromator was used for the conventional XAFS measurements of the Ti K-edge (4965 eV). Two Rh-coated mirrors were used for the vertical focusing and the elimination of the higher-order harmonics.

In the dispersive optics, a curved crystal of Si(111) was used for making the dispersive X rays in the Bragg configuration. The polychromator was bent horizontally by leading movements at the both fixed sides of the crystal. The crystal was cooled by soaking in an In-Ga pool. The focus point of the dispersed X rays corresponding to the sample position was set to 1000 mm from the polychromator. A phosphor screen (10 μm thick Gd₂O₂S(Tb)) was exposed to the dispersed X rays from the sample and emitted lights were collected using a charge coupled device (CCD) camera (640 × 480 channels, 12 bits). The intensities in the vertical direction (about 200 channels) were summed to enable a one-dimensional spectroscopy. The horizontal focus size of the X rays was measured to be 0.05 mm in full width at half maximum (FWHM) and the vertical size is equal to the sample pellet height for accumulating the intensity of transmitted X rays. Two Rh-coated mirrors were used in the same way as the conventional setup. In the dispersive measurement, only the X-ray absorption near-edge structure (XANES) spectra were obtained because of high intensity of the higher-order harmonics at the energy of the Ti K-edge in the SPring-8 ring and the low linearity of the detector, especially phosphor screen.

All spectra were recorded in the transmission mode. The samples (about 5 mg) were mixed with boron nitride matrix (20 mg) by a mortar in about 10 minutes under He atmosphere. Homogeneously dispersed samples were pressed to make a pellet (φ = 7 mm). The pellets were attached to the sample cell filled with He gas. During XAFS measurements, He gas was always flowed in the sample cell to avoid exposing to air. XAFS spectra were taken with an acquisition time of about 60 minutes and 10 seconds for conventional and dispersive mode, respectively. During continuous measurement of thermal desorption analysis, samples were heated from room temperature to 500 °C with a constant rate of 10 K/min. Desorbed hydrogen during XAFS monitoring was observed by QMS.

3. Results

3.1 TiCl₃ additive to Mg(BH₄)₂

3.1.1 Conventional XAFS analyses

Figure 1(a) shows the Ti K-edge XANES spectra of 2 mol% TiCl₃ additive in Mg(BH₄)₂. This figure indicates that 2 mol% TiCl₃ additive has already converted to other compound just after the ball milling mixture even at the room temperature. By heating the sample, the drastic change is observed between 25°C and 250°C. Then, the shape of the spectra keeps same until 500°C. The similar tendency is observed in the case of 10 mol% TiCl₃ addition (Fig. 1(b)), though the change of the spectra is not so drastic as the case of the 2 mol% TiCl₃ addition.

Fourier transform intensities of k³-weighted extended X-ray absorption fine structure (EXAFS) spectra are summarized in Fig. 2 as well as the fitted curves. Estimated EXAFS parameters are shown in Table 1. The fitting parameters were coordination number (CN), interatomic distance (R), edge energy shift and mean square relative displacement (C²). For the standard spectra, simulated results from FEFF 8.4 code were used.

As for the 2 mol% and 10 mol% TiCl₃ additives, a similar trend is observed in Figs. 2(a) and 2(b), which means that structural transformation occurs between 25 and 250°C. This is consistent with the change of the XANES spectra seen in Figs. 1(a) and 1(b). For the TiCl₃ addition samples, judging from the value of interatomic distance, the nearest-neighbor peak is a result of boron coordination. Determined interatomic distance of the nearest-neighbor Ti-B bonding indicates that the samples have shorter distances of Ti-B bonding at 25°C (2.11–2.12 Å) than those at higher temperature (2.35–2.41 Å). The interatomic distance of Ti-B bonding is 2.375 Å for TiB₂ and 2.201 Å for Ti(BH₄)₃ in literature, this suggests that borohydride sample can show a shorter interatomic distance than boride sample. It is reasonable to consider that the nearest-neighbor peak of Fourier transform intensities of TiCl₃ additives at 25°C is assigned to titanium-related borohydride, which is probably expressed as TiₓMg₁₋ₓ/₂(BH₄)₂ (x = 0–0.67).
Elongated Ti-B interatomic distance observed at higher temperature is considered to originate in the formation of TiB$_2$, which is estimated by the similarity of the bond length. Boride formation by heating was also pointed out in the cobalt chloride addition system, but in that case, they reported that the cobalt chloride was converted to metal cobalt phase by ball milling procedure. For the TiCl$_3$ addition sample, some other peaks are observed in the Fourier transform intensities. The analysis under the supposition that residuals of left TiCl$_3$ and reduced Ti metal are contained reproduces the experimental spectra well. Ti metal component still exists in the higher temperature.

3.1.2 Dispersive XAFS + QMS analyses

In order to study the correlation between the local structure of Ti additives and the dehydrogenation mechanism, the simultaneous and continuous observation of the local structure of Ti atoms by dispersive XAFS and the dehydrogenation curve by QMS was operated. At first, as the typical information, the Ti K-edge XANES spectra obtained by the dispersive XAFS system were depicted in Fig. 3. Because of the high intensity of higher-order harmonics at the photon energy of Ti K-edge, the XANES spectra show many irregular jumps and dips. Nevertheless, these jumps and dips originate from the position dependence of the light intensity, these irregular jumps and dips do not change during monitoring XAFS spectra. The uneven curves in XANES spectra may hinder the precise observation of the small peak of XANES curve, but in the case of observation for the

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**Table 1** EXAFS parameters determined from the fitting seen in Fig. 2. Range of the Fourier transform is typically 3–10 Å$^{-1}$. Fitting was performed in the $R$-space with a typical range of 0.5–2.5 Å (2 mol% TiCl$_3$), 0.5–2.8 Å (10 mol% TiCl$_3$) and 0.5–2.0 Å (2 mol% TiO$_2$). The intrinsic loss factor was estimated to be 0.7 from a Ti foil at room temperature.

<table>
<thead>
<tr>
<th>Additive</th>
<th>$T$ (°C)</th>
<th>shell</th>
<th>$CN$</th>
<th>$R$ (Å)</th>
<th>$C_2$ (0.01 Å$^2$)</th>
<th>$R$-fac. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 mol% TiCl$_3$</td>
<td>25</td>
<td>B</td>
<td>1.9(3)</td>
<td>2.12(1)</td>
<td>0.4(2)</td>
<td>2.0</td>
</tr>
<tr>
<td>250</td>
<td>B</td>
<td>8.9(30)</td>
<td>2.41(4)</td>
<td>1.4(5)</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>B</td>
<td>10.1(15)</td>
<td>2.39(1)</td>
<td>1.6(2)</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>10 mol% TiCl$_3$</td>
<td>25</td>
<td>B</td>
<td>2.9(7)</td>
<td>2.11(2)</td>
<td>0.9(3)</td>
<td>1.5</td>
</tr>
<tr>
<td>250</td>
<td>B</td>
<td>7.2(7)</td>
<td>2.37(1)</td>
<td>1.2(1)</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>B</td>
<td>2.1(2)</td>
<td>3.02(1)</td>
<td>1.2(1)**</td>
<td>0.8 **</td>
<td></td>
</tr>
<tr>
<td>10 mol% TiO$_2$</td>
<td>25</td>
<td>O</td>
<td>6.0(4)</td>
<td>1.96(1)</td>
<td>0.5(1)</td>
<td>0.4</td>
</tr>
<tr>
<td>250</td>
<td>O</td>
<td>5.3(3)</td>
<td>1.96(1)</td>
<td>0.5(1)</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>O(B)</td>
<td>7.3(15)</td>
<td>2.04(2)</td>
<td>1.9(4)</td>
<td>1.5</td>
<td></td>
</tr>
</tbody>
</table>

*Fixed values obtained from the reference samples.
**Same parameter with B shell.

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Fig. 2 Fourier transform intensities of $k^3$-weighted EXAFS functions for Mg(BH$_4$)$_2$ + (a) 2 mol% TiCl$_3$, (b) 10 mol% TiCl$_3$ and (c) 2 mol% TiO$_2$ additives. Dotted lines indicate the fitted ones.

Fig. 3 Ti K-edge XANES spectra for Mg(BH$_4$)$_2$ + 2 mol% TiCl$_3$ obtained from the dispersive optics at 25°C (solid circle) and 500°C (open circle). Exposure time of each spectroscopy is 10 seconds.
relative shift of spectra, we can receive the advantage of the dispersive XAFS optics that serves stable and fast monitoring because of the unmoving optical mechanism. By fitting the XANES spectra with the simple step function, we obtain the relative shift of the absorption edge position for the Ti additives. Although the XANES spectra contain many fine peaks at the edge energy position, such easy approach is still useful for studying the dynamic information by the continuous observation.

The edge energy shift of the Ti additives from the continuous measurement of the Ti K-edge XANES spectra by the dispersive XAFS optics is summarized in Fig. 4 as well as the dehydrogenation curves obtained by the simultaneous measurement of QMS. In the case of the 2 mol% TiCl₃ addition sample shown in Fig. 4(a), the edge energy shift shows the abrupt change at 100–150 °C, which indicates the structural change of the Ti compound occurs around 100–150 °C. After that, no critical change is observed until 500 °C. The very small peak at 100–150 °C and the large peak at 350 °C are distinguished in the dehydrogenation curve. The main peak originates from the dehydrogenation reaction of Mg(BH₄)₂. Recent study has indicated that Mg(BH₄)₂ itself shows the three dehydrogenation peaks between 300 and 380 °C, as shown in Fig. 4(d). In this study, lower resolution of the QMS system produces the single peak at 350 °C.

By comparing the dehydrogenation curve of the 10 mol% TiCl₃ addition sample shown in Fig. 4(b) with the 2 mol% TiCl₃ addition sample, it is indicated that the peak at 100–150 °C is much enhanced in the 10 mol% TiCl₃ addition sample. This is consistent with the recent result which has reported the growth of the peak at 100–150 °C as the increase of amount of TiCl₃ additive. As for the absorption edge energy, the abrupt change of the edge energy position seems to be related to the peak of the dehydrogenation curve at 100–150 °C. On the other hand, the absorption energy shift does not show the change at 350 °C where the main peak of the hydrogen desorption curve appears. The 10 mol% TiCl₃ addition sample shows opposite direction of the edge energy shift compared with the 2 mol% TiCl₃ addition sample. As seen in the Fig. 1, the shape of XANES spectra of the 10 mol% TiCl₃ addition sample at 25 °C do not resemble much that of the 2 mol% addition sample. The intersection energy of XANES spectra between 25 °C and higher temperature locates at the middle of edge jump in the 10 mol% TiCl₃ addition sample, which indicates that a simple analysis of edge energy position can be shifted to either direction. However, because the structure change of Ti additive occurs at the same temperature, we consider that the correlation between local structural change of Ti and dehydrogenation property is similar in both samples. The 10 mol% TiCl₃ addition sample contains TiₓMg₁₋ₓ/2(BH₄)ₓ, TiCl₃, and metallic Ti, which can influence the shift style of absorption edge due to the change of ratio of components. As a result, we have concluded that the local structural change of the Ti compound is directly related to the first dehydrogenation peak at 100–150 °C, and is not much influenced by the main dehydrogenation peak at 350 °C. Both of the dehydrogenation peak and the change of the Ti K-edge absorption energy position at 100–150 °C originate from the dehydrogenation reaction of TiₓMg₁₋ₓ/2(BH₄)ₓ. At higher temperature, TiₓMg₁₋ₓ/2(BH₄)ₓ is converted to TiB₂ which is more stable compound and keeps its structure until 500 °C.

3.2 TiO₂ additive to Mg(BH₄)₂

3.2.1 Conventional XAFS analyses

The local structure of Ti atoms for 2 mol% TiO₂ additive in Mg(BH₄)₂ shows different character with the case of the TiCl₃ additive. Figure 1(c) indicates that the local structure of Ti atoms just after the ball milling mixture is the same with the start compound of TiO₂. The structure of TiO₂ is kept till 250 °C by heating. However, the spectra show difference at 500 °C. This indicates that TiO₂ is converted between 250 and 500 °C. By comparing the case of the TiCl₃ addition, TiO₂ is more stable compound than TiCl₃ during the ball milling mixture with Mg(BH₄)₂. Moreover, TiO₂ shows more stability for thermal activation than the case of TiCl₃ addition because the TiO₂ kept its structure even at 250 °C.
3.2.2 Dispersive XAFS + QMS analyses

A peak in the preedge region was observed in the titanium at the preedge region. In the past study, a similar single sharp peak in titanium(IV) isopropoxide has Ti-O with a width of the dehydrogenation curve at 350°C. 

Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also addition. Different reaction mechanism between titanium(IV) chloride and titanium(III) chloride was also add