

Dehydriding reaction of AlH_3 : *in-situ* microscopic observations combined with thermal and surface analyses

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Abstract. The dehydriding reaction of a single phase of $\alpha\text{-AlH}_3$ was investigated by *in-situ* microscopic observations combined with thermal and surface analyses. Before the dehydriding reaction, primary AlH_3 particles with sizes of 100 nm–1 μm were suggested to be covered by an oxide layer with a thickness of less than 5 nm. Both the precipitation/grain-growth of metallic Al with sizes of 1–50 nm and an increase in “boundary space” were clearly observed inside the particles, while the morphologies of the particles covered by the layer did not change during the dehydriding reaction. This preliminary report provides fundamental information for a further study of AlH_3 as a possible hydrogen storage material.

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1. Introduction

Aluminium trihydride (AlH_3 , alane) has been recently investigated as a possible hydrogen storage material because of its high gravimetric and volumetric hydrogen densities (10 mass% and $149 \text{ kgH}_2/\text{m}^3$, respectively) and also of a simple dehydriding reaction ($\text{AlH}_3 \rightarrow \text{Al} + 3/2\text{H}_2$) at 370–470 K [1–3]. Among the variations of its crystalline structure [4–10], $\alpha\text{-AlH}_3$ is the most stable, in which the enthalpy change of the dehydriding reaction is in the range of -5.7 to -7.6 kJ/molH_2 [3, 11, 12]. This range indicates that the equilibrium hydrogen pressure of $\alpha\text{-AlH}_3$ is around 1 GPa at 298 K. A surface layer that is apparently composed of oxides is present on AlH_3 particles, which prevents the occurrence of the dehydriding reaction of “ AlH_3 ” to Al at room temperature [11–13]. It is of great importance to precisely study the nanostructures of the surface layer and inside of the AlH_3 particles using microscope techniques [14]. In this study, therefore, we attempted to elucidate the nanostructure of the AlH_3 particles with the single phase of $\alpha\text{-AlH}_3$ during the dehydriding reaction by *in-situ* microscopic observations combined with thermal and surface analyses.

2. Experimental

AlH_3 particles were prepared by the chemical reaction between LiAlH_4 and AlCl_3 in ether solution [3, 6, 15, 16]; the particles were then examined by thermogravimetry analysis (TG, heating rate of 1 K/min under He) and powder X-ray diffraction measurement (XRD, Cu $\text{K}\alpha$ radiation). The particles were dispersed on a carbon tape and microgrid mesh for *in-situ* scanning electron microscopy (SEM, JEOL JSM6009, 3 kV) and transmission electron microscopy (TEM, JEOL JEM2100 with a Gatan ES500W Erlangshen CCD high-speed camera, 100 kV) observations, respectively. The TEM observations were performed under an electron flux of approximately 2×10^5 electrons/ nm^2s for avoiding a damage of the particles by electron irradiation. A pellet of the particles was prepared for X-ray photoelectron spectroscopy (XPS, VG EscaLab spectrometer with SPECS PHOIBOS 100 analyzer, Mg $\text{K}\alpha$ radiation, base pressure better than 10^{-9} mbar).

3. Results and discussion

Figure 1 shows the TG profile and SEM images during the dehydriding reaction of the AlH_3 particles. The TG profile shows that the dehydriding reaction starts at around 370 K and the amount of desorbed hydrogen is 9.6 ± 0.2 mass% (corresponding to 96% of the ideal amount in AlH_3 , 10.1 mass%). From the XRD profiles shown in figure 2, we can also confirm the existence of the single phase of $\alpha\text{-AlH}_3$ with a molecular volume of $33.4 \text{ \AA}^3/\alpha\text{-AlH}_3$ and metallic Al with a molecular volume of $16.6 \text{ \AA}^3/\text{Al}$ before and after the dehydriding reaction, respectively. The two-fold shrinkage in molecular volume from $\alpha\text{-AlH}_3$ to metallic Al was highly expected to cause a change in the morphologies of the primary particles. The SEM images, however, indicate that the morphologies of the particles with sizes of 100 nm–1 μm do not change at all during the dehydriding reaction, as also shown in figure 1(a)–(c).

TEM image of the primary AlH_3 particles before the dehydriding reaction is shown in figure 3(a), and the particles are found to have sizes of around 100–200 nm. The electron diffraction pattern shown in figure 4 suggests that the particle before the dehydriding reaction is the single crystal of $\alpha\text{-AlH}_3$ that exhibits the “Kikuchi pattern”. The particles are covered by a surface layer (probably composed of oxides, described later) with a thickness of less than 5 nm.

Furthermore, the TEM images during the dehydriding reaction (heating achieved by electron irradiation) are shown in figure 3(b)–(f). Clearly, nanoscale (~ 1 nm) precipitations can be observed inside the primary particles with sizes of around 100–200 nm, then, these precipitations exhibit the continuous grain-growth (20–50 nm). Simultaneously, the “boundary space” in the primary particles increases because of the shrinkage in the molecular volume from $\alpha\text{-AlH}_3$ to metallic Al, as described above. The electron diffraction pattern shown in figure 4 indicates the existence of the polycrystalline metallic Al after the dehydriding reaction; it may be noted that the polycrystals were formed from the single crystal of AlH_3 during the dehydriding reaction. On the surface layer, neither the formation of cracks nor a change in thickness was observed during the dehydriding reaction.

It was, therefore, found that the surface morphology of the primary AlH_3 particles was not affected by the dehydriding reaction; however the nanostructure inside the particles was found to change drastically by the precipitations and their continuous grain-growth of the metallic Al.

Figure 5 shows the XPS profile of the primary AlH_3 particles before the dehydriding reaction. Apart from small contaminations by carbon, contributions from only O and Al are observed. Further investigations by XPS combined with thermal analyses, which are comparable to investigations of the MgH_2 particles [17], are currently in progress.

As described in the introduction section, the surface layer on the primary AlH_3 particles should play a dominant role against the occurrence of the dehydriding reaction (thereby retaining the “ AlH_3 ” structure inside of the particles) at room temperature. Further, the metallic Al after the dehydriding reaction will have intrinsic effects on the re-hydriding reaction, for example, under high hydrogen pressure [18–22]. Thus, this preliminary report on nanostructure observations during the dehydriding reaction provides fundamental information for further studies of AlH_3 as a possible hydrogen storage material.

4. Conclusions

We attempted to elucidate the changes of the primary AlH_3 particles with the single phase of $\alpha\text{-AlH}_3$ during the dehydriding reaction. The particles with sizes of 100 nm–1 μm appear to be covered by an oxide layer with a thickness of less than 5 nm before the dehydriding reaction. The morphology of the particles covered by the surface layer does not change during the dehydriding reaction because there is neither an observable formation of cracks nor a change in the thickness of the surface layer during the reaction. On the other hand, both the precipitation/grain-growth of the polycrystalline metallic Al with sizes of 1–50 nm and an increase in the “boundary space” were clearly observed inside the particles.

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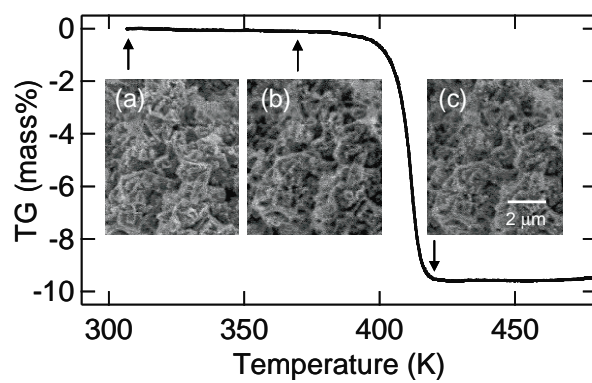


Figure 1. Thermogravimetry (TG) profile of the AlH₃ particles. Insets show *in-situ* SEM images; (a) before the dehydriding reaction and during the reaction at (b) 370 K and (c) 420 K.

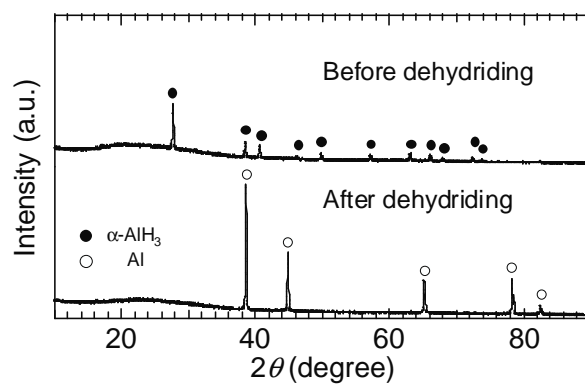


Figure 2. Powder XRD profiles of the AlH₃ particles before and after the dehydriding reactions. The broad up-hill of 10–30 degree is coming from the glass plate for the measurement.

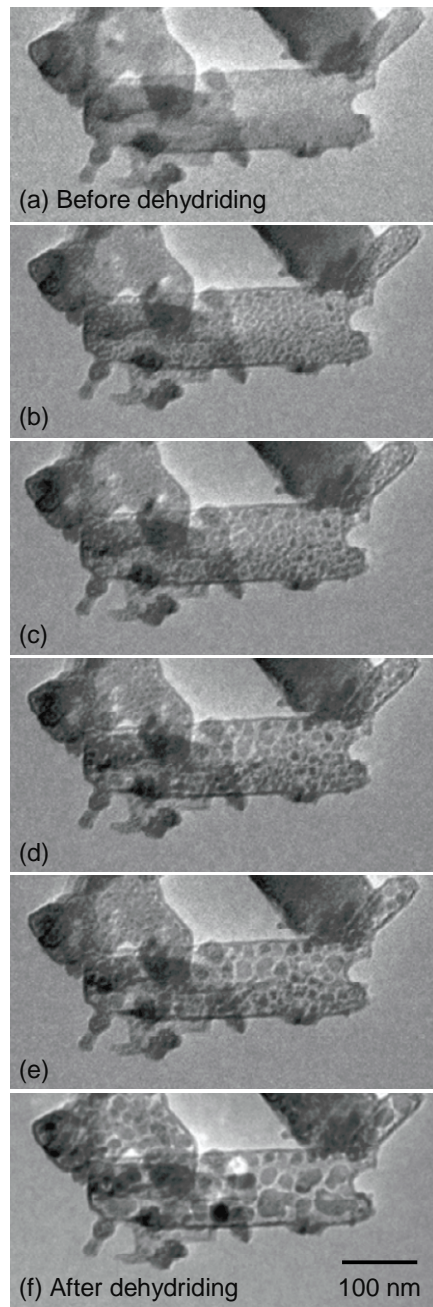


Figure 3. TEM images of the primary AlH_3 particles (a) before and (b)-(f) during/after the dehydriding reactions.

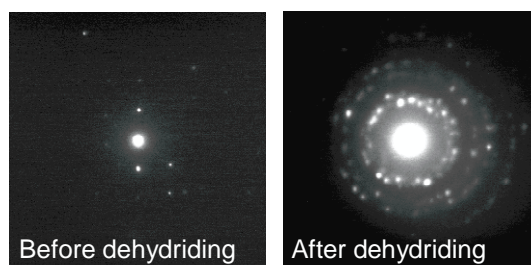


Figure 4. Electron diffraction patterns from the areas in figure 3(a) and (f).

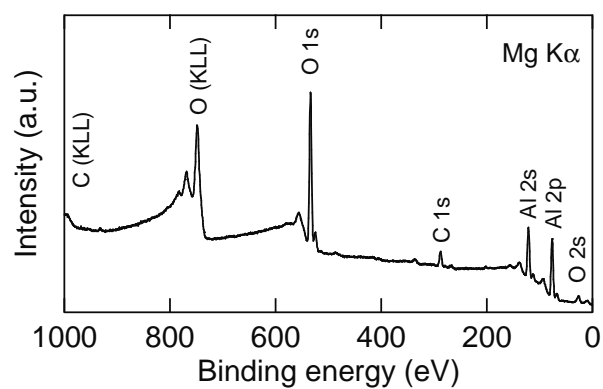


Figure 5. X-ray photoelectron spectroscopy (XPS) profile of the primary AlH_3 particles before the dehydrating reaction.