



Title	Doping effect of Nb species on hydrogen desorption properties of AlH <sub>3</sub>
Author(s)	Nakagawa, Yuki; Lee, Chung-Hyun; Matsui, Kouki; Kousaka, Kohei; Isobe, Shigehito; Hashimoto, Naoyuki; Yamaguchi, Shotaro; Miyaoka, Hiroki; Ichikawa, Takayuki; Kojima, Yoshitsugu
Citation	Journal of alloys and compounds, 734, 55-59 <a href="https://doi.org/10.1016/j.jallcom.2017.10.273">https://doi.org/10.1016/j.jallcom.2017.10.273</a>
Issue Date	2018-02-15
Doc URL	<a href="http://hdl.handle.net/2115/76747">http://hdl.handle.net/2115/76747</a>
Rights	© 2018. This manuscript version is made available under the CC-BY-NC-ND 4.0 license <a href="http://creativecommons.org/licenses/by-nc-nd/4.0/">http://creativecommons.org/licenses/by-nc-nd/4.0/</a>
Rights(URL)	<a href="http://creativecommons.org/licenses/by-nc-nd/4.0/">http://creativecommons.org/licenses/by-nc-nd/4.0/</a>
Type	article (author version)
File Information	3rd draft.pdf



[Instructions for use](#)

# Doping effect of Nb species on hydrogen desorption properties of AlH<sub>3</sub>

Yuki Nakagawa<sup>a\*</sup>, Chung-Hyun Lee<sup>a</sup>, Kouki Matsui<sup>a</sup>, Kohei Kousaka<sup>a</sup>, Shigehito Isobe<sup>a</sup>, Naoyuki Hashimoto<sup>a</sup>, Shotaro Yamaguchi<sup>b</sup>, Hiroki Miyaoka<sup>c</sup>, Takayuki Ichikawa<sup>d</sup>, Yoshitsugu Kojima<sup>c</sup>

<sup>a</sup> Graduate School of Engineering, Hokkaido University, N-13, W-8, Sapporo, 060-8278, Japan

<sup>b</sup> Graduate School of Advanced Sciences of Matter, and <sup>c</sup> Natural Science Center for Basic Research and Development, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima, 739-8530, Japan

<sup>d</sup> Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima, 739-8527, Japan.

## ABSTRACT:

Hydrogen desorption properties of  $\alpha$ -AlH<sub>3</sub> doped with Nb species (Nb, Nb<sub>2</sub>O<sub>5</sub> and NbF<sub>5</sub>) were investigated. Doping Nb species improved the desorption properties of AlH<sub>3</sub>. In particular, 1 mol% NbF<sub>5</sub>-doped AlH<sub>3</sub> showed the lowest onset desorption temperature at 60 °C. Compared with Nb- or Nb<sub>2</sub>O<sub>5</sub>-doped AlH<sub>3</sub>, the fine distribution of dopant was successfully achieved in NbF<sub>5</sub>-doped AlH<sub>3</sub>. The apparent activation energy for hydrogen desorption of AlH<sub>3</sub> was slightly decreased with the dopant of NbF<sub>5</sub>. The improvement of desorption properties might be due to the finely dispersed Nb and/or AlF<sub>3</sub>, which are formed by the reaction between NbF<sub>5</sub> and AlH<sub>3</sub> (surface Al<sub>2</sub>O<sub>3</sub>).

Keywords: Hydrogen storage; Aluminum hydride, Niobium Fluoride, Niobium oxide, Catalytic effect

## Introduction

Aluminum hydride ( $\text{AlH}_3$ ) is an ideal off-board hydrogen storage material because of its high hydrogen capacities (10.1 mass% and 149 g  $\text{H}_2/\text{L}$ ) and low desorption temperature ( $<100\text{ }^\circ\text{C}$ ) [1]. However, its desorption kinetics is not enough to meet the targets for practical applications [2]. Although  $\text{AlH}_3$  is thermodynamically metastable at room temperature, it has been suggested that the surface  $\text{Al}_2\text{O}_3$  film on  $\text{AlH}_3$  particle would inhibit the spontaneous decomposition at room temperature [3]. Ball-milling can enhance the desorption kinetics of  $\text{AlH}_3$ , likely due to an increase of oxide free surfaces on  $\text{AlH}_3$  particles [3,4]. However, the mechanistic study showed that the real reason for the enhancement would be the small amount of desorption during ball-milling [5,6]. The formation of metallic Al particles on the hydride surface would serve as channels for the enhanced desorption and reduce the incubation period [5,6]. In addition, doping additives is one of the common strategies to enhance the kinetics of  $\text{AlH}_3$ . For instance, the enhanced desorption properties have been reported for the reactive hydride composites between  $\text{AlH}_3$  and other compounds ( $\text{MgH}_2$  [7,8],  $\text{LiBH}_4$  [9],  $\text{MgCl}_2$  [10] *etc.*). Also, Ti is a well-known and effective catalyst for  $\text{AlH}_3$ . The measurable enhancement of kinetics was observed by doping  $\text{TiCl}_3$  with just a few ppm levels in solution during the  $\text{AlH}_3$  synthesis [6].

Nb-based additives have been considered as effective dopants to improve hydrogen sorption reactions of hydrogen storage materials. For instance,  $\text{Nb}_2\text{O}_5$  is a well-known catalyst for hydrogen absorption and desorption reactions of  $\text{MgH}_2$  [11-14]. The composite,  $\text{MgH}_2$  and 1 mol%  $\text{Nb}_2\text{O}_5$  milled for 20 h, was able to absorb -4.5 mass% of hydrogen within 15 s at room temperature under lower pressure than 1.0 MPa and desorb -6.0 mass% of hydrogen at  $160\text{ }^\circ\text{C}$  [12]. Also,  $\text{NbF}_5$  is also an effective dopant for various kinds of hydrogen storage materials, such as  $\text{MgH}_2$  [15,16], alanate [17,18] and borohydride [19] system. The composite,  $\text{MgH}_2$  and 2 mol%  $\text{NbF}_5$  milled for 5 h, was able to absorb -5.0 mass% of hydrogen in 12 s and desorb -4.4

mass% of hydrogen in 10 min at 300 °C [15]. Hydrogen desorption properties of MgH<sub>2</sub>-AlH<sub>3</sub> nanocomposites were investigated in the previous study, where the addition of just 1 mol% NbF<sub>5</sub> remarkably destabilized  $\gamma$ -AlH<sub>3</sub> in the composite and led to its decomposition at room temperature [8]. Other fluorides, such as CeF<sub>4</sub> [20] and TiF<sub>4</sub> [21], were also effective additives to enhance the kinetics of MgH<sub>2</sub>.

Thus, the addition of Nb-based additives showed the improvements of de/absorption properties of hydrogen storage materials. However, the effect of Nb-based additives on  $\alpha$ -AlH<sub>3</sub> (the most stable phase of AlH<sub>3</sub>) has not been reported. In the present study, Nb, Nb<sub>2</sub>O<sub>5</sub>, and NbF<sub>5</sub> (hereinafter called “Nb species”) were doped with  $\alpha$ -AlH<sub>3</sub>. Then, their hydrogen desorption properties and distribution states of Nb species were analyzed. In addition, the chemical bonding states of Nb and F were further investigated in the NbF<sub>5</sub>-doped AlH<sub>3</sub> in order to clarify the reaction process.

## **Experimental Section**

### **Sample Synthesis**

Commercially available Nb (Kojundo Chemical Lab., 99.99 %), Nb<sub>2</sub>O<sub>5</sub> (Kojundo Chemical Lab., 99.99 %), NbF<sub>5</sub> (Sigma Aldrich, 98 %) and AlF<sub>3</sub> (Sigma Aldrich, 99.9 %) were used as-received for this research. AlH<sub>3</sub> was prepared by the chemical reaction between LiAlH<sub>4</sub> and AlCl<sub>3</sub> in ether solution [22]. The samples were prepared by ball-milling AlH<sub>3</sub> and Nb species using a planetary ball-mill apparatus (Fritsch Pulverisette 7) with 21 g of stainless balls and 100 mg samples. The milling was performed under 0.1 MPa Ar with 200 rpm for 1 h with two cycles of 30/15 min operation/interval per each cycle. All material handlings were conducted under in a glovebox filled with purified Ar gas in order to avoid oxidation.

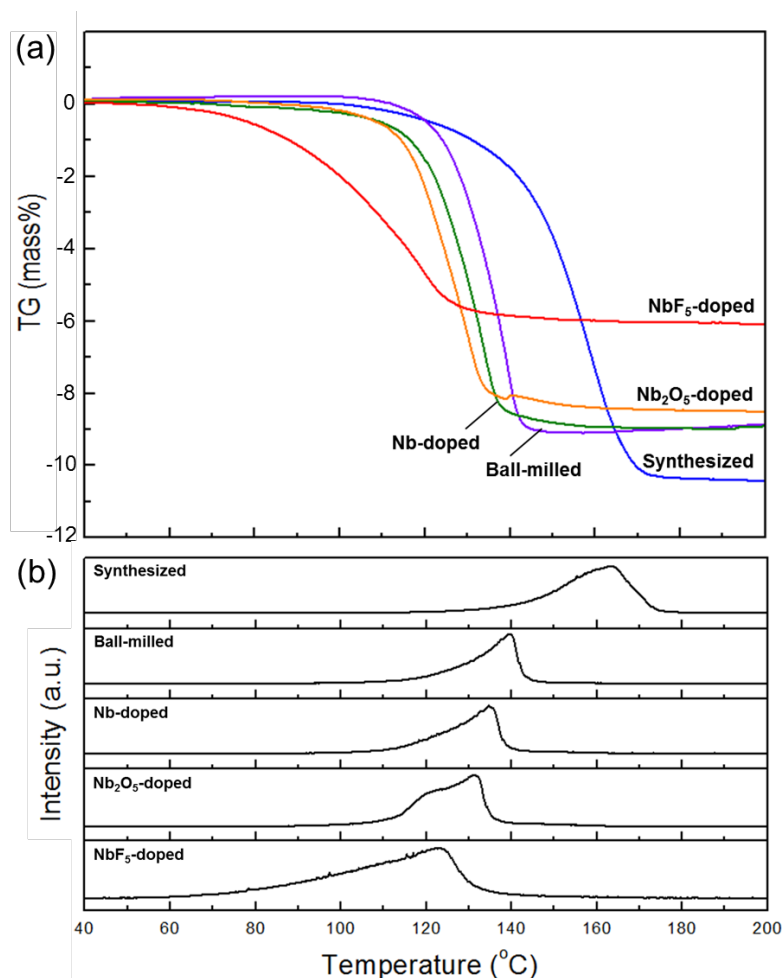
### **Characterization**

Hydrogen desorption properties were examined by a thermogravimetry and differential thermal analysis equipment (TG-DTA, Bruker 2000SA) connected to a mass spectrometer (MS, ULVAC, BGM-102). The desorbed gases were carried from TG-DTA equipment to MS through a capillary by flowing high purity He gas as a carrier gas. The flow rate of He gas was set to 300 mL min<sup>-1</sup>. The samples were heated from room temperature to 200 °C with a heating rate of 5 °C min<sup>-1</sup>. The crystalline phases of samples were analyzed by powder X-ray diffraction (XRD, PANalytical, X'Pert-Pro with Cu K $\alpha$  radiation). The samples for XRD were placed on a glass plate in a glovebox and then covered with a polyimide sheet and sealed by grease in order to avoid the oxidation during the measurement. SEM-EDS measurements were performed to observe the distribution states of Nb species by using JIB-4600F/HKD, JEOL. The chemical bonding states of samples were studied by using X-ray Photoelectron Spectroscopy (XPS, Thermo Fisher Scientific, ESCALab 250Xi) with Al K $\alpha$  radiation.

## **Results and discussion**

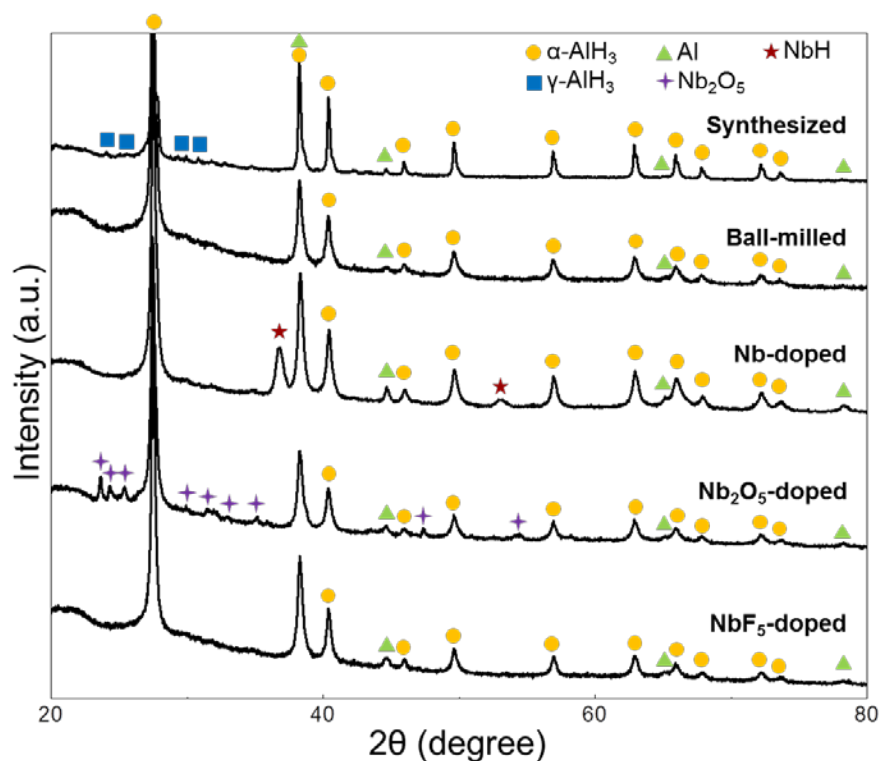
### **Doping effect of Nb species**

Fig. 1 shows the hydrogen desorption properties of as-synthesized, ball-milled, and Nb species-doped AlH<sub>3</sub>. As shown in Fig. 1(a) and (b), the hydrogen desorption temperature was reduced after ball-milling and doping with Nb species. The kinetic enhancement in the ball-milled AlH<sub>3</sub> would originate from the formation of metallic Al particles on the hydride surface as shown in the “Introduction” part. In fact, the mass loss of ball-milled AlH<sub>3</sub> (-9 mass%) was lower than that of as-synthesized AlH<sub>3</sub> (-10 mass%), suggesting the formation of metallic Al nuclei during ball-milling. It seemed that Nb- and Nb<sub>2</sub>O<sub>5</sub>-doped AlH<sub>3</sub> showed the improvement of the desorption kinetics compared with ball-milled one. Among all the samples, NbF<sub>5</sub>-doped AlH<sub>3</sub> showed the



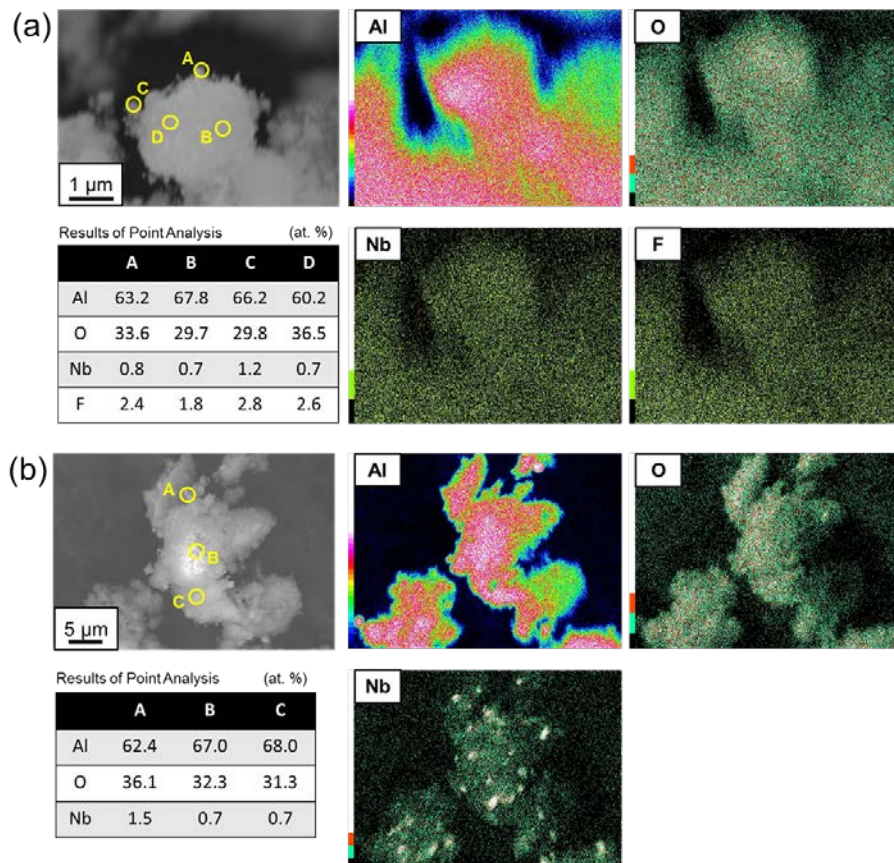
**Fig. 1** (a) TG profiles and (b) MS ( $m/z = 2$ , H<sub>2</sub>) profiles of as-synthesized, ball-milled, and Nb-, Nb<sub>2</sub>O<sub>5</sub>-, NbF<sub>5</sub>-doped AlH<sub>3</sub>. The amount of Nb species was 1 mol% in each doped sample. The heating rate was 5 °Cmin<sup>-1</sup>. The mass loss value was calculated by using the total system mass.

lowest desorption temperature. It started to desorb hydrogen from 60 °C with a peak temperature at 122 °C (Fig.1(b)). However, the hydrogen mass loss of NbF<sub>5</sub>-doped AlH<sub>3</sub> was only -6 mass%, whose value was the smallest among all the samples. We also measured the sample with 5 mol% NbF<sub>5</sub> doping, but most of the hydrogen was released during ball-milling (The desorbed hydrogen amount during heating was only -1 mass%). Thus, doping a large amount of NbF<sub>5</sub> promoted the decomposition during ball-milling.



**Fig. 2** XRD patterns of as-synthesized, ball-milled, and Nb-, Nb<sub>2</sub>O<sub>5</sub>-, NbF<sub>5</sub>-doped AlH<sub>3</sub>. The amount of Nb species was 1 mol% in each doped sample.

Fig. 2 shows the XRD patterns of samples. Although as-synthesized sample contained  $\alpha$ -AlH<sub>3</sub> and a small amount of  $\gamma$ -AlH<sub>3</sub>, ball-milled one did not contain  $\gamma$ -AlH<sub>3</sub>, probably due to its transformation to  $\alpha$ -AlH<sub>3</sub> during milling [23]. The formation of NbH was observed in the Nb-doped AlH<sub>3</sub>, indicating Nb reacted with AlH<sub>3</sub> during ball-milling. In the Nb<sub>2</sub>O<sub>5</sub>-doped AlH<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub> was observed after milling. In the case of MgH<sub>2</sub> doped with Nb<sub>2</sub>O<sub>5</sub>, reduced Nb<sub>2</sub>O<sub>5-x</sub> phase was found on the surface of the samples [24]. Thus, the surface state of Nb<sub>2</sub>O<sub>5</sub> could be also changed in the Nb<sub>2</sub>O<sub>5</sub>-doped AlH<sub>3</sub> system. On the other hand, Nb- or F-containing phases were not observed in any of the diffraction patterns of the NbF<sub>5</sub>-doped AlH<sub>3</sub>. In order to investigate the distribution states of Nb dopants, SEM-EDS measurements were conducted for NbF<sub>5</sub>- and Nb<sub>2</sub>O<sub>5</sub>-doped AlH<sub>3</sub> (Fig. 3). As shown in Fig. 3(a), micron-particles containing Nb or F were not observed from the EDS mapping images. Similar results were obtained in the case of

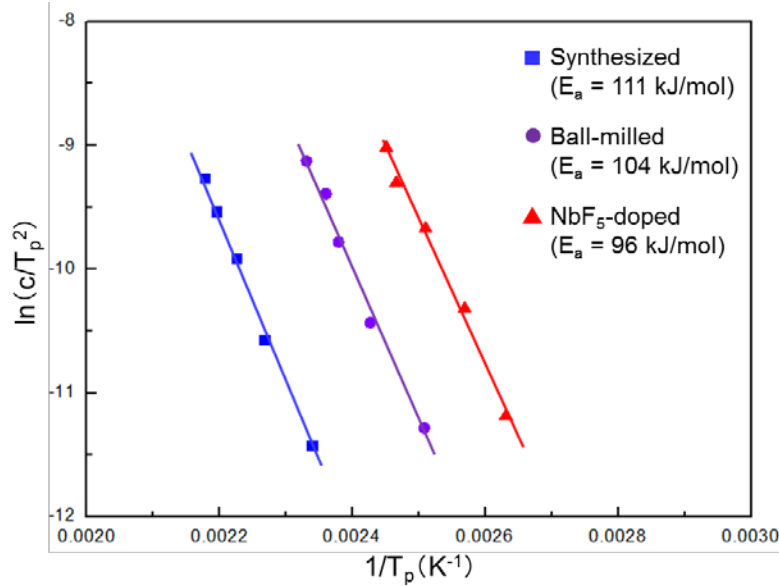


**Fig. 3** SEM-EDS results of (a) 1 mol% NbF<sub>5</sub>-doped AlH<sub>3</sub> and (b) 1 mol% Nb<sub>2</sub>O<sub>5</sub>-doped AlH<sub>3</sub>. Secondary-electron images and EDS results (point analysis and mapping images) are shown.

5 mol% NbF<sub>5</sub> doping. On the other hand, the micron-particles containing Nb and O were clearly observed in the Nb<sub>2</sub>O<sub>5</sub>-doped AlH<sub>3</sub>. Thus, it seemed that Nb and F distributed uniformly on the surface of AlH<sub>3</sub> in the NbF<sub>5</sub>-doped AlH<sub>3</sub>. The fine distribution of Nb and F was also observed in other NbF<sub>5</sub>-doped hydride systems [8,25,26]. For instance, Kim *et al.* suggested that NbF<sub>5</sub> will melt during ball-milling and this promoted the presence of extremely fine Nb/NbH film on the surface of MgH<sub>2</sub> particles in NbF<sub>5</sub>-doped MgH<sub>2</sub> system [25,26]. Thus, compared with Nb- or Nb<sub>2</sub>O<sub>5</sub>-doped AlH<sub>3</sub>, the fine distribution of dopant was successfully achieved in the NbF<sub>5</sub>-doped AlH<sub>3</sub>.



## Investigation of NbF<sub>5</sub>-doped AlH<sub>3</sub>

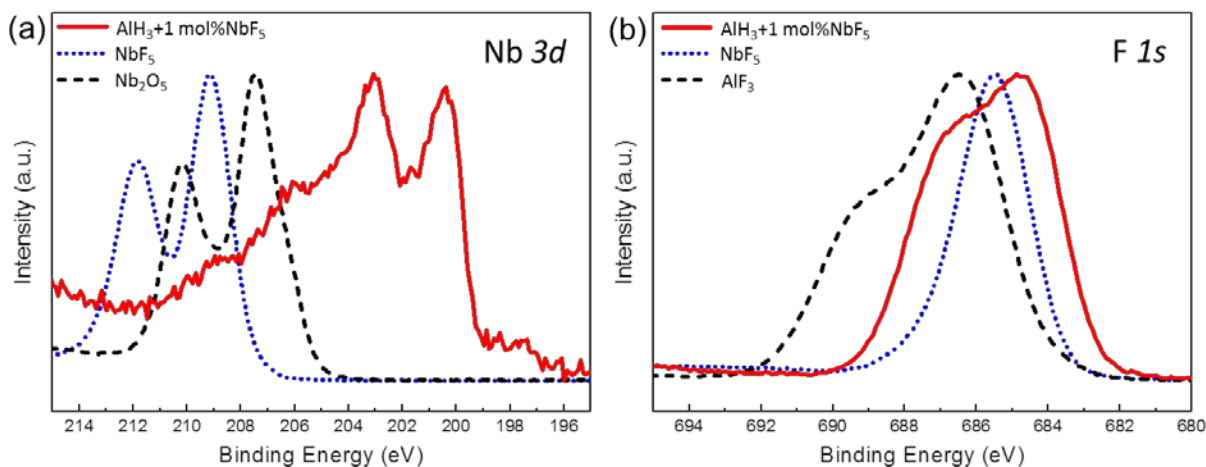


**Fig. 4** Kissinger plots for hydrogen desorption of as-synthesized, ball-milled and 1 mol% NbF<sub>5</sub>-doped AlH<sub>3</sub>.

In order to get an insight on the desorption mechanism, further investigation was conducted for the NbF<sub>5</sub>-doped AlH<sub>3</sub>, which showed the lowest onset temperature among all the samples. The activation energy for hydrogen desorption was analyzed for the NbF<sub>5</sub>-doped AlH<sub>3</sub>. Fig. 4 shows the Kissinger plots for the hydrogen desorption of AlH<sub>3</sub> and NbF<sub>5</sub>-doped AlH<sub>3</sub>. The apparent activation energy for hydrogen desorption is calculated by using Kissinger equation [27],

$$\ln \frac{c}{T_p^2} = -\frac{E_a}{RT_p} + \ln \frac{RA}{E_a}$$

where  $E_a$  is the apparent activation energy for hydrogen desorption,  $c$  is the heating rate,  $T_p$  is the peak temperature,  $R$  is gas constant, and  $A$  is the frequency factor. The activation energies of as-synthesized AlH<sub>3</sub>, ball-milled AlH<sub>3</sub>, and NbF<sub>5</sub>-doped AlH<sub>3</sub> were calculated to be 111, 104, and 96 kJ/mol, respectively. The values for as-synthesized and ball-milled AlH<sub>3</sub> were similar to those

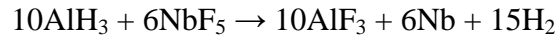


**Fig. 5** XPS spectra of (a) Nb  $3d$  and (b) F  $1s$  regions of 1 mol%  $\text{NbF}_5$ -doped  $\text{AlH}_3$ . The spectra of  $\text{NbF}_5$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{AlF}_3$  are also shown as references.

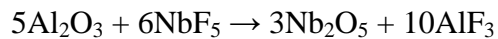
of the previous study (104 kJ/mol [5], 102 kJ/mol [28]). The activation energy of  $\text{NbF}_5$ -doped  $\text{AlH}_3$  was just slightly decreased compared with as-synthesized and ball-milled  $\text{AlH}_3$ . As shown in the “Introduction” part, Ti is known as an effective catalyst for  $\text{AlH}_3$ . It was reported that a decrease of the activation energy by at least 50 % is possible with the addition of Ti [6]. Thus, the effect of Nb on the decomposition kinetics would be less pronounced than that of Ti. The effect of cation species on the kinetics should be further clarified to understand the catalytic mechanism of hydrogen desorption from  $\text{AlH}_3$ .

The bonding states of Nb and F elements were studied by using XPS. For comparison, the standard materials of  $\text{NbF}_5$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{AlF}_3$  were also measured. Fig. 5(a) shows the XPS spectra of Nb  $3d$  region. In the  $\text{NbF}_5$ -doped  $\text{AlH}_3$ , the binding energies of Nb  $3d_{3/2}$  and  $3d_{5/2}$  shift towards to the chemical states of Nb, suggesting the reaction between  $\text{NbF}_5$  and  $\text{AlH}_3$  would occur to form Nb. Also, shoulder peaks appeared between 204.0-212.0 eV, suggesting the presence of Nb oxide species *e.g.*,  $\text{Nb}_2\text{O}_5$  and/or NbO. Fig. 5(b) shows the XPS spectra of F  $1s$  region. In the  $\text{NbF}_5$ -doped  $\text{AlH}_3$ , the binding energies of F  $1s$  peaks were observed at 686.5 eV

(AlF<sub>3</sub>) and a new peak at 684.8 eV. The new peak position is similar to the previously reported AlF<sub>x</sub>O<sub>y</sub> species [29], suggesting such kind of AlF<sub>x</sub>O<sub>y</sub> phase could exist. The broad peak at 688.9 eV in the starting material of AlF<sub>3</sub> might be attributed to the contamination of C-F species [30]. The XPS results suggest that the following reaction would occur during the milling process:



whose Gibbs free energy  $\Delta G^\circ = -3570.4$  kJ [31,32] is possible from the thermodynamic potentials. The Nb spectrum in the NbF<sub>5</sub>-doped AlH<sub>3</sub> (Fig.5 (a)) was similar to that of NbF<sub>5</sub>-doped MgH<sub>2</sub> system [15]. In this system, MgF<sub>2</sub> and Nb were formed by the reaction between MgH<sub>2</sub> and NbF<sub>5</sub>. Thus, the chemical state of Nb was similar between AlH<sub>3</sub> and MgH<sub>2</sub> system. However, the existence of oxide species (Nb oxide, AlF<sub>x</sub>O<sub>y</sub>) could be one of the characteristics in the AlH<sub>3</sub> system. It is known that amorphous- or  $\chi$ -Al<sub>2</sub>O<sub>3</sub> film exists on the surface of AlH<sub>3</sub> particles [33,34]. Due to the lack of the standard Gibbs free energy of formation for amorphous- or  $\chi$ -Al<sub>2</sub>O<sub>3</sub>, we considered the reaction with the most stable phase,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, as follows:



whose Gibbs free energy  $\Delta G^\circ = -1442.2$  kJ [31] is thermodynamically possible. Thus, NbF<sub>5</sub> could also react with surface Al<sub>2</sub>O<sub>3</sub> film in the NbF<sub>5</sub>-doped AlH<sub>3</sub> system. In order to clarify the detailed catalytic mechanism, *e.g.*, *in-situ* measurements on the reaction process between NbF<sub>5</sub> and surface Al<sub>2</sub>O<sub>3</sub> film should be conducted. As the summary of XPS results, the formation of finely dispersed Nb species and/or AlF<sub>3</sub> could have the catalytic effect for hydrogen desorption of AlH<sub>3</sub>. According to the previous study, AlF<sub>3</sub>-doped AlH<sub>3</sub> led to the decomposition of AlH<sub>3</sub> at room temperature [35], suggesting AlF<sub>3</sub> may have such catalytic effect.

## **Conclusion**

In summary, the addition of Nb species (Nb, Nb<sub>2</sub>O<sub>5</sub>, NbF<sub>5</sub>) enhanced the hydrogen desorption properties of  $\alpha$ -AlH<sub>3</sub>. In particular, 1 mol% NbF<sub>5</sub>-doped AlH<sub>3</sub> started to desorb hydrogen from 60 °C with a peak temperature at 122 °C. Compared with Nb- or Nb<sub>2</sub>O<sub>5</sub>-doped AlH<sub>3</sub>, the fine distribution of dopant was observed in the NbF<sub>5</sub>-doped AlH<sub>3</sub>. The activation energy for hydrogen desorption was slightly decreased by doping NbF<sub>5</sub>. From the XPS analysis, the reactions between NbF<sub>5</sub> and AlH<sub>3</sub> (surface Al<sub>2</sub>O<sub>3</sub> film) were suggested. The improvement in the NbF<sub>5</sub>-doped AlH<sub>3</sub> might be ascribed to the formation of finely distributed Nb and/or AlF<sub>3</sub>.

## **AUTHOR INFORMATION**

### **Corresponding Author**

\* Corresponding author. Tel.: +81 11 706 6769; Fax: +81 11 706 6772.

E-mail addresses: y-nakagawa@eng.hokudai.ac.jp (Y. Nakagawa)

### **Acknowledgements**

A part of this work was conducted at “Joint-Use Facilities: Laboratory of Nano-Micro Material Analysis” at Hokkaido University, supported by the “Material Analysis and Structure Analysis Open Unit (MASAOU)” and “Nanotechnology Platform” Program of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

### **References**

[1] J. Graetz, ISRN Materials Science 2012 (2012) 863025.

- [2] J. Graetz, J. J. Reilly, J. G. Kulleck, R. C. Bowman, *J. Alloys Comp.* 446-447 (2007) 271-275.
- [3] G. Sandrock, J. Reilly, J. Graetz, W. M. Zhou, J. Johnson, J. Wegrzyn, *J. Alloys Comp.* 421 (2006) 185-189.
- [4] Y. Nakagawa, S. Isobe, Y. Wang, N. Hashimoto, S. Ohnuki, L. Zeng, S. Liu, T. Ichikawa, Y. Kojima, *J. Alloys Comp.* 580 (2013) S163-S166.
- [5] I. Gabis, M. Dobrotvorskiy, E. Evard, A. Voyt, *J. Alloys Comp.* 509S (2011) S671-S674.
- [6] J. Graetz, J. J. Reilly, V. A. Yartys, J. P. Maehlen, B. M. Bulychev, V. E. Antonov, B. P. Tarasov, I. E. Gabis, *J. Alloys Comp.* 509S (2011) S517-S528.
- [7] H. Liu, X. Wang, Y. Liu, Z. Dong, H. Ge, S. Li, M. Yan, *J. Phys. Chem. C* 118 (2014) 37-45.
- [8] H. Liu, X. Wang, Y. Liu, Z. Dong, S. Li, H. Ge, M. Yan, *J. Phys. Chem. C* 118 (2014) 18908-18916.
- [9] H. Liu, X. Wang, H. Zhou, S. Gao, H. Ge, S. Li, M. Yan, *Int. J. Hydrogen Energy* 41 (2016) 22118-22127.
- [10] C. W. Duan, L. X. Hu, Y. Sun, H. P. Zhou, H. Yu, *Phys. Chem. Chem. Phys.* 17 (2015) 22152-22159.
- [11] G. Barkhordarian, T. Klassen, R. Bormann, *J. Alloys Comp.* 364 (2004) 242-246.
- [12] N. Hanada, T. Ichikawa, S. Hino, H. Fujii, *J. Alloys Comp.* 420 (2006) 46-49.
- [13] T. Ma, S. Isobe, Y. Wang, N. Hashimoto, S. Ohnuki, *J. Phys. Chem. C* 117 (2013) 10302-10307.
- [14] T. Kimura, H. Miyaoka, T. Ichikawa, Y. Kojima, *Int. J. Hydrogen Energy* 38 (2013) 13728-13733.
- [15] Y. Luo, P. Wang, L. P. Ma, H. M. Cheng, *J. Alloys Comp.* 453 (2008) 138-142.

- [16] N. Recham, V. V. Bhat, M. Kandavel, L. Aymard, J. M. Tarascon, A. Rougier, *J. Alloys Comp.* 464 (2008) 377-382.
- [17] M. Ismail, Y. Zhao, X. B. Yu, S. X. Dou, *Int. J. Hydrogen Energy* 35 (2010) 2361-2367.
- [18] J. Mao, Z. Guo, H. Liu, *Int. J. Hydrogen Energy* 36 (2011) 14503-14511.
- [19] H. Kou, G. Sang, Y. Zhou, X. Wang, Z. Huang, W. Luo, L. Chen, X. Xiao, G. Yang, C. Hu, *Int. J. Hydrogen Energy* 39 (2014) 11675-11682.
- [20] H. J. Lin, J. Matsuda, H. W. Li, M. Zhu, E. Akiba, *J. Alloys Comp.* 645 (2015) S392-S396.
- [21] M. Jangir, A. Jain, S. Yamaguchi, T. Ichikawa, C. Lal, I. P. Jain, *Int. J. Hydrogen Energy* 41 (2016) 14178-14183.
- [22] F. M. Brower, N. E. Matzek, P. F. Reigler, H. W. Rinn, C. B. Rovers, D. L. Schmidt, J. A. Snover, K. Terada, *J. Am. Chem. Soc.* 98 (1976) 2450-2453.
- [23] S. Orimo, Y. Nakamori, T. Kato, C. Brown, C. M. Jensen, *Appl. Phys. A* 83 (2006) 5-8.
- [24] T. Ma, S. Isobe, E. Morita, Y. Wang, N. Hashimoto, S. Ohnuki, T. Kimura, T. Ichikawa, Y. Kojima, *Int. J. Hydrogen Energy* 36 (2011) 12319-12323.
- [25] J. W. Kim, J. P. Ahn, S. A. Jin, S. H. Lee, H. S. Chung, J. H. Shim, Y. W. Cho, K. H. Oh, *J. Power Sources* 178 (2008) 373-378.
- [26] J. W. Kim, J. P. Ahn, D. H. Kim, H. S. Chung, J. H. Shim, Y. W. Cho, K. H. Oh, *Scr. Mater.* 62 (2010) 701-704.
- [27] H. E. Kissinger, *Anal. Chem.* 29 (1957) 1702-1706.
- [28] J. Graetz, J. J. Reilly, *J. Phys. Chem. B* 109 (2005) 22181-22185.
- [29] X. Wu, P. Cong, S. Mori, *Appl. Surf. Sci.* 201 (2002) 115-122.
- [30] A. Limcharoen, C. Pakpum, P. Limsuwan, *Procedia Engineering* 32 (2012) 1043-1049.

- [31] D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, R. L. Nuttall, *J. Phys. Chem. Ref. Data* 11 (1982) Suppl. 2.
- [32] J. Graetz, J. Reilly, G. Sandrock, J. Johnson, W. M. Zhou, J. Wegrzyn, Brookhaven National Laboratory Formal Report BNL-77336-2006 (2006).
- [33] S. Muto, K. Tatsumi, K. Ikeda, S. Orimo, *J. Appl. Phys.* 105 (2009) 123514.
- [34] K. Ikeda, H. Ohshita, N. Kaneko, J. Zhang, M. Yonemura, T. Otomo, K. Suzuya, H. Yukawa, M. Morinaga, H. W. Li, S. Semboshi, S. Orimo, *Mater. Trans.* 52 (2011) 598-601.
- [35] J. E. Fonnelløp, M. Corno, H. Grove, E. Pinatel, M. H. Sørby, P. Ugliengo, M. Baricco, B. C. Hauback, *J. Alloys Comp.* 509 (2011) 10-14.