In Situ X-Ray Diffraction Measurement of Hydrogenation and Dehydrogenation of Aluminum at High Pressure and Temperature

Hydrogen is the ideal energy carrier since it can avert adverse effects on the environment and reduce dependence on imported oil for countries without natural resources. The safe and efficient storage of hydrogen is widely considered as one of the key technological challenges to realizing a hydrogen-based energy economy. Hydrogen can be store as pressurized gas, cryogenic liquid, and solid fuel in chemical or physical combinations with other materials; hydrogen forms metal hydrides with some metals and alloys leading to solid-state storage that provides the important advantage of safety over the gas and liquid storage methods.

AlH_3 is a metal hydride with the highest hydrogen content (10.1 mass%) and therefore is a promising candidate for hydrogen storage material. AlH_3 has been synthesized only by a desolvation reaction after the chemical reaction between $LiAlH_4$ and $AlCl_3$ in ether [1,2] and was shown to crystallize in seven polymorphs. In order to utilize AlH_3 as a practical energy source, it is necessary to develop a more efficient synthesis route. The hydrogenation of aluminum metal is the simplest method of synthesizing AlH_3. Thermodynamic studies show an equilibrium H_2 pressure of around 1 GPa at room temperature for the α phase, the most stable phase under ambient conditions. It is hence ruled out to synthesize AlH_3 from aluminum metal by the conventional hydrogenation technique using hydrogen gas pressurized up to 10 MPa, which is much lower than the estimated equilibrium pressure of 1 GPa. Understanding the simple hydrogenation reaction is indispensable to developing other synthetic methods for AlH_3. Herein, we attempted to hydrogenate pristine aluminum at high temperature and high pressure to clarify the hydrogenation mechanism of aluminum. The hydrogenation and decomposition processes were observed by *in situ* X-ray diffraction measurement [3].

High-pressure and high-temperature environments were generated with a cubic-type multi-anvil apparatus installed at beamline **BL14B1**. A schematic of the *in situ* X-ray diffraction measurement system and high-pressure cell is shown in Fig. 1. Highly pure aluminum (Nilaco Corporation, Japan, purity 6N) disks punched from 50-μm-thick foil were stacked to fill a pyrolytic boron nitride capsule 0.8 mm in diameter and 0.4 mm in length, and then placed in a hydrogen sealing capsule along with an internal hydrogen source. The aluminum foil was used as received. A photoelectron spectroscopy measurement indicated that the oxide layer was 35 Å thick. Incident X-rays were collimated to 50 μm × 300 μm square on the sample and diffracted X-rays were measured with a germanium solid-state detector mounted on a goniometer.

The sample was compressed to 10.0 GPa and then heated from room temperature to 600 °C at a rate of 10 °C/min. The hydrogen source decomposed at around 300 °C to supply free hydrogen, which condensed into hydrogen fluid and immersed the metal sample to be hydrogenated. The Bragg peak, which was assigned to the 012 reflection of α-AlH_3, appeared at 600 °C. The hydrogenation of pristine aluminum began at the pressure-temperature conditions. The pristine passivated aluminum foil was not hydrogenated at pressures below 7.5 GPa under pressure and temperature conditions at which α-AlH_3 is thermodynamically stable.

Figure 2 shows the temperature variation of X-ray diffraction profiles of the hydrogenated aluminum

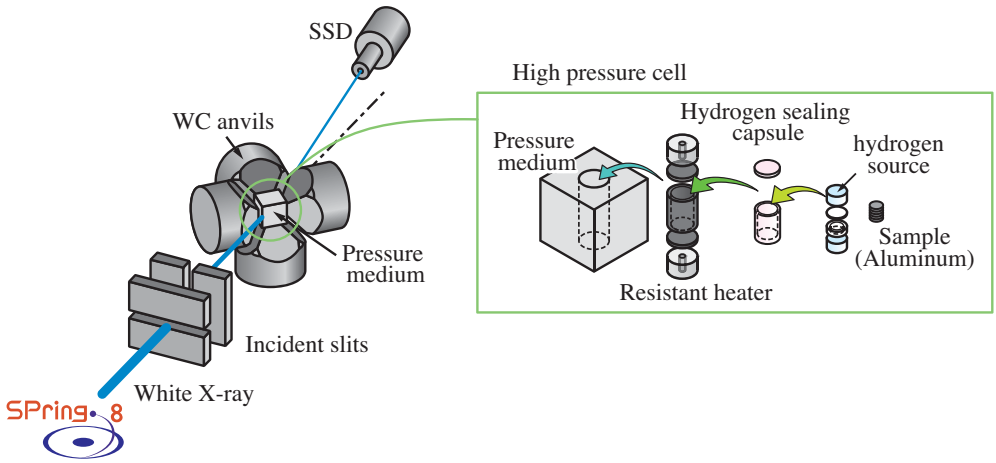

Fig. 1. Schematic of *in situ* X-ray diffraction measurement system and high-pressure cell.

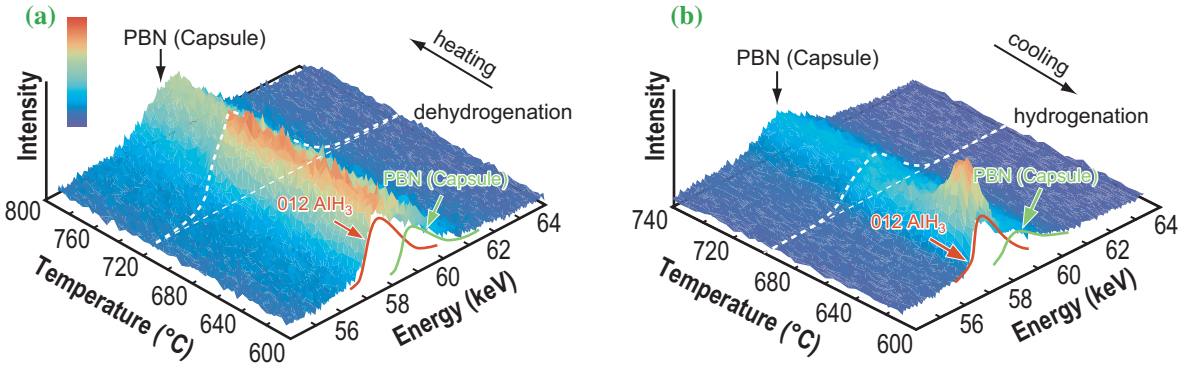

Fig. 2. Temperature variation of X-ray diffraction profiles taken at 10.0 GPa during **(a)** heating and **(b)** cooling.

taken at 10.0 GPa. When the sample was heated to 720 °C, 012 reflection of α-AlH_3 and other Bragg peaks from α-AlH_3 (these are not shown in Fig. 2) vanished; α-AlH_3 was dehydrogenated. These peaks reappeared upon successive cooling; aluminum was hydrogenated again to form α-AlH_3 .

After aluminum was hydrogenated at 10 GPa and the dehydrogenation-hydrogenation reaction was repeated, cyclic dehydrogenation and hydrogenation processes were observed at pressures lower than 7.5 GPa. The pressure-temperature diagram of the hydrogen-aluminum system was determined (Fig. 3). In the present study, all the hydrogenated aluminum has the α-AlH_3 structure, confirming that α-AlH_3 is the most stable phase. This activation effect for hydrogenation suggests the possibility of synthesizing AlH_3 under more moderate conditions, even below 4 GPa.

The hydride crystals thus prepared at high pressure and temperature were recovered under ambient conditions. They were colorless and transparent (Fig. 3 inset), and the grain size ranged roughly from a few to 50 mm. These grains were expected to be single crystals on the basis of polarized micrograph observation. The powder X-ray diffraction pattern of the recovered AlH_3 was measured. All the Bragg peaks can be indexed with the unit cell of α-AlH_3. Traces of other AlH_3 polymorphs were not found. The single phase of α-AlH_3 was obtained. EDS analysis did not detect impurities.

We succeeded in the hydrogenation of pristine aluminum with hydrogen fluid at high temperature and high pressure, and the recovery of AlH_3 crystals under ambient conditions. This synthesis method allows the preparation of a large amount of single crystals of AlH_3. The obtained single crystals will be useful for characterizing the thermodynamic and kinetic properties of AlH_3 as well as for studying the bonding nature. *In situ* X-ray diffraction measurement will be further applicable to a study of the dynamics of the hydrogenation and dehydrogenation cycles, which will lead to the improvement of the high-pressure synthesis method. The synthesis of aluminum-rich metal hydrides is being carried out at SPring-8.

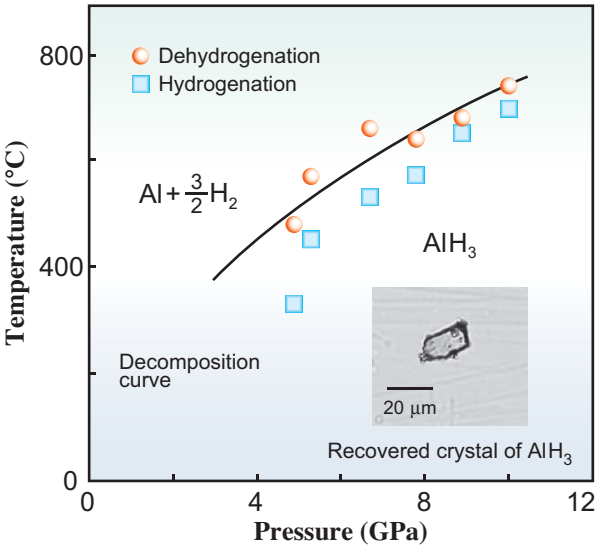

Fig. 3. Hydrogenation and dehydrogenation pressure-temperature conditions determined by *in situ* X-ray diffraction measurements. Inset shows a micrograph of a recovered AlH_3 crystal.

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References

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