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***In situ* X-ray diffraction measurement of the hydrogenation and dehydrogenation of aluminum and characterization of the recovered AlH_3**

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Abstract. Pristine aluminum was hydrogenated to form AlH_3 at 8.9 GPa and 600 °C. The cyclic formation and decomposition of the hydride were measured by *in situ* synchrotron X-ray diffraction measurement. AlH_3 synthesized under high pressure and temperature was recovered at ambient conditions. The recovered AlH_3 was characterized by conventional powder X-ray diffraction measurement and Raman spectroscopy. The results of the characterization were consistent with that obtained for chemically prepared AlH_3 and indicated that single phase α - AlH_3 was obtained.

1. Introduction

Hydrogen is an ideal energy carrier since it minimizes harmful effects on the environment. Development of a safe and efficient storage of hydrogen is widely considered as one of the key technological challenges to realize a hydrogen-based energy economy. Hydrogen can be stored as a pressurized gas, cryogenic liquid and solid fuel in which hydrogen is chemically or physically combined with other materials. For example, hydrogen forms metal hydrides with some metals and alloys leading to solid-state storage which provide the safety advantage over the gas and liquid storage method.

AlH_3 is a metal hydride with the largest hydrogen content (10.1% by mass), and is therefore a promising candidate as a hydrogen storage material. AlH_3 has been synthesized only by organometallic synthetic routes [1,2]. Previous studies suggest the possibility of direct hydrogenation of aluminum metal above 0.7 GPa on the basis of the van't Hoff relation. However, hydrogenation of pristine aluminum has failed even at pressures as high as 2.5 GPa[3] due to passivation of aluminum in air to form a chemically stable oxide layer.

Recently, we have succeeded in demonstrating the hydrogenation of passivated aluminum, and the recovery of AlH_3 [4,5]. Hydrogen fluid becomes extremely reactive at high pressure and temperature (around 9 GPa and 600 °C), and enables hydrogenation of passivated aluminum. In the present paper we show the result of *in situ* synchrotron X-ray diffraction measurements on hydrogenation and dehydrogenation of aluminum under high pressure and temperature. The recovered AlH_3 was characterized by conventional powder X-ray diffraction and Raman measurements.

2. Experimental

High-pressure and high-temperature environments were generated with a cubic-type multi-anvil apparatus installed in beamline BL14B1 at SPring-8[6]. Highly pure aluminum (Nilaco Corporation, Japan, purity 6N) disks punched from a 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[7,8]. The stack of foils was used instead of bulk sample of pure aluminum, because only its surface was hydrogenated when we used bulk sample. The gaps between the aluminum foils were expected to work as hydrogen transmitting path and increase the yield of AlH_3 . The aluminum foils were used as received. A photoelectron spectroscopy measurement estimated that the oxide layer was 35 \AA thick. The aluminum sample was compressed to the desired pressure (around 10 GPa) and then heated to the preset temperature (around 600 $^\circ\text{C}$).

Reactions of the sample were observed by synchrotron radiation X-ray diffraction measurements. Incident X-rays were collimated to 50 μm x 300 μm in a square geometry on the sample, and the diffracted X-rays were measured by a germanium solid-state detector mounted on a goniometer. AlH_3 samples prepared at high pressure and temperature were recovered at ambient conditions and characterized by powder X-ray diffraction measurements (Rigaku R-Axis Rapid) and energy-dispersive spectroscopy (EDS) analysis with a scanning electron microscope (JEOL JSM-5310LV and JED-2140).

Raman spectra of the recovered AlH_3 were measured at both ambient and high pressures. The spectra were acquired at wavenumbers between 200 and 1000 cm^{-1} . The incident laser beam (diode-pumped solid-state laser with the wavelength of 532 nm) was focused onto a spot size of 10 μm . A diamond anvil cell (DAC) with diamonds of 500- μm culet size was used to generate high pressure during Raman measurements. Powder samples were placed in a 160- μm hole in a 80 μm -thick stainless steel gasket together with ruby chips for pressure measurements. KBr was used as the pressure-transmitting medium.

3. Result and discussion

3.1. *In situ* X-ray diffraction measurement on hydrogenation and dehydrogenation of aluminum

The sample was compressed to 8.9 GPa and then heated to 600 $^\circ\text{C}$ at a rate of 10 $^\circ\text{C}/\text{min}$. The internal hydrogen source emitted hydrogen fluid at about 300 $^\circ\text{C}$. Aluminum was immersed in the hydrogen fluid to form its hydride. However, aluminum was not hydrogenated below 600 $^\circ\text{C}$ at 8.9 GPa because the oxide layer prevented hydrogenation. The Hydrogenation of aluminum was observed above 600 $^\circ\text{C}$.

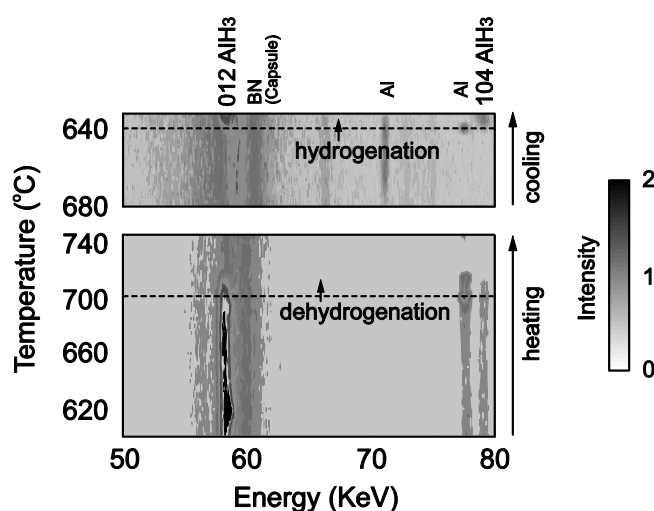


Figure 1. Temperature variation of X-ray diffraction profiles taken at 8.9 GPa.

Figure 1 shows the temperature variation of X-ray diffraction profiles of the hydrogenated aluminum taken at 8.9 GPa. When the sample was heated to 700 °C, all the Bragg peaks from AlH_3 vanished indicating that the AlH_3 was dehydrogenated. These peaks reappeared upon successive cooling as the aluminum re-hydrogenated. Cyclic dehydrogenation and hydrogenation processes were observed above 8.9 GPa.

The pristine passivated aluminum was not hydrogenated below 6.5 GPa due to its stable oxide layer. However, once passivated aluminum experienced hydrogenation-dehydrogenation cycles, it became reactive with hydrogen and was hydrogenated below 6.5 GPa. Hydrogenation and dehydrogenation conditions were obtained for the activated aluminum by *in situ* X-ray diffraction measurements [4]. While the hydrogenation temperature agreed with the previously reported equilibrium curve [10], the decomposition temperatures were about 100 °C higher than the equilibrium temperatures.

3.2. Characterization of the recovered AlH_3

The recovered AlH_3 sample was characterized by powder X-ray diffraction measurement and the obtained diffraction pattern is shown in figure 2. Unreacted aluminum (about a half volume of the recovered sample) was eliminated for the measurement. All the Bragg peaks can be indexed with a hexagonal unit cell of $\alpha\text{-AlH}_3$ [9]; traces of other AlH_3 polymorphs were not found. EDS analysis did not detect impurities indicating that single-phase pure $\alpha\text{-AlH}_3$ was formed.

Figure 3 shows the results of Raman measurements at ambient pressure. There are two strong Raman peaks at 509.9 and 720.9 cm^{-1} . Though a weak peak at around 850 cm^{-1} was indistinct (which was detected on another measurement without DAC), the positions of the strong Raman peaks agree with those reported by Tkacz et al. [11]. As the pressure increased, the Raman peaks shifted to higher wavenumbers. The peak positions of the Raman spectra as function of the pressure are plotted in figure 4. These results are consistent with the previous reports [11]. No difference has been detected between AlH_3 obtained by high-pressure synthesis and that by the organometallic synthetic route.

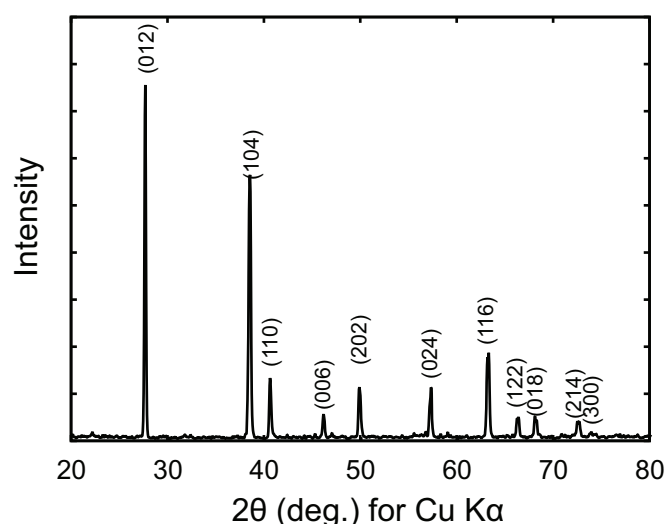


Figure 2. Powder X-ray diffraction pattern of the recovered AlH_3 .

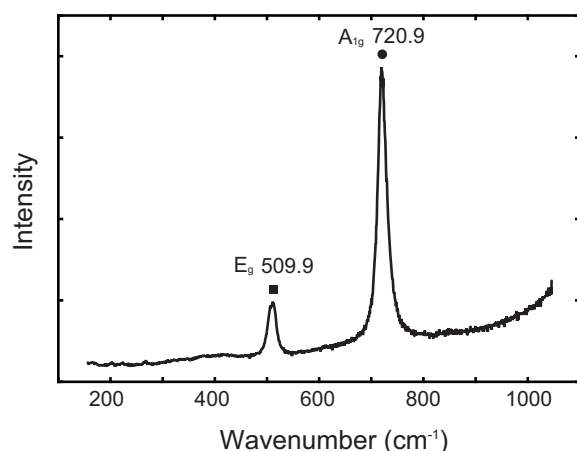


Figure 3. Raman spectrum from the recovered AlH_3 . Symbols on the peaks correspond to figure 4.

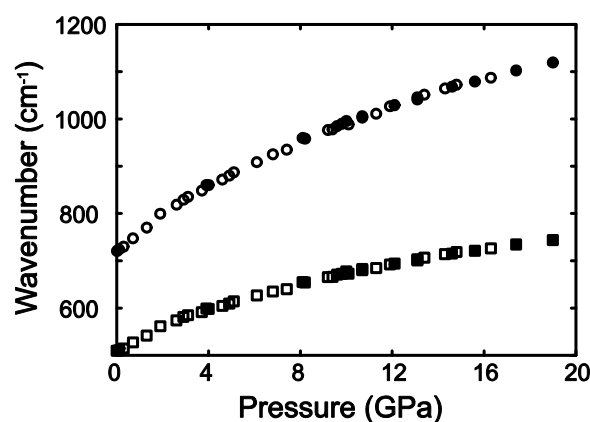


Figure 4. The peak positions of the Raman spectra as a function of the pressure on compression (filled symbols) and decompression (open symbols)

4. Conclusions

We have succeeded in demonstrating the hydrogenation of pristine passivated aluminum with hydrogen fluid at 8.9 GPa and 600 °C, and the recovery of AlH_3 crystals at ambient conditions. It was confirmed that the recovered AlH_3 was highly-pure single-phase $\alpha\text{-AlH}_3$ by powder X-ray diffraction measurements, EDS analysis, and Raman spectroscopy. This synthetic method allows preparation of large amounts of AlH_3 , even in single-crystal form. The obtained AlH_3 will be useful to reveal the thermodynamic and kinetic properties of the hydrogenation and dehydrogenation of aluminum. *In situ* X-ray diffraction measurement will be further applicable to the dynamics study of hydrogenation and dehydrogenation cycles, which will lead to improvements in high-pressure synthesis.

Acknowledgments

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