Hydrogenation of Al$_3$Ti at High Pressure and High Temperature

Hiroyuki Saitoh*, Akihiko Machida, Yoshinori Katayama and Katsutoshi Aoki

Condensed Matter Science Division, Quantum Beam Science Directorate, Japan Atomic Energy Agency, Sayo-gun, Hyogo 679-5148, Japan

An Al$_3$Ti alloy was immersed in hydrogen at high pressures and high temperatures. An anomalous expansion of the Al$_3$Ti metal lattice was observed by in situ powder X-ray diffraction measurements at 625°C and 10 GPa, suggesting that Al$_3$Ti is hydrogenated to form Al$_3$TiH$_x$. The hydrogen content is roughly estimated to be $x \approx 0.4$. However, the formed hydride phase is dehydrogenated during depressurization, and cannot be recovered at ambient conditions. [doi:10.2320/matertrans.MA201006]

Keywords: aluminum-titanium-hydride, high pressure and high temperature

1. Introduction

Aluminum hydride (AlH$_3$) has attracted much attention due to its low dehydrogenation temperature (~100°C) and low dehydrogenation enthalpy as well as its high gravimetric (10 mass%) and volumetric (148 kg/m$^3$) hydrogen content.$^{1-6}$ AlH$_3$ has been produced mainly via organometallic synthetic routes. AlH$_3$ is thermodynamically unstable at ambient conditions; high pressures above 4.5 GPa are necessary to hydrogenate passivated aluminum,$^{7-9}$ which limits practical applications of AlH$_3$ as a hydrogen storage material.

Aluminum alloy hydrides have been studied to use lightweight aluminum as a hydrogen storage material instead of AlH$_3$. Issob et al. have reported Mg substitution of AlH$_3$ by ball milling a mixture of $(1-x)$AlH$_3$/xMgH$_2$. More-\overline{ver}$^{10}$, some groups have reported different crystal structures for aluminum alloy hydrides from AlH$_3$. These hydrides are synthesized near ambient pressure. Novel aluminum alloy hydrides are expected to be prepared under high pressure in which passivated aluminum can react with hydrogen fluid.

The present study demonstrates the hydrogenation reaction of an Al$_3$Ti alloy at high pressures and high temperatures as an example hydrogenation reaction of aluminum-based alloys. Herein the reactions are monitored by in-situ synchrotron radiation X-ray diffraction measurements.

2. Experimental

The starting material was Al$_3$Ti alloy, which was prepared by a reaction between pure aluminum (purity 2N, NewMet, UK) and pure titanium (purity 3N, Nilaco, Japan) powders at 1.0 GPa and 1000°C for 20 min. The alloy was identified as a single phase Al$_3$Ti intermetallic compound by a powder X-ray diffraction measurement.$^{13}$ The crystal structure of Al$_3$Ti was a superstructure derived from face-centered cubic (FCC) aluminum.

The specimens were immersed in hydrogen fluid at high pressures and high temperatures. These pressure-temperature conditions were far higher than those of supercritical point of hydrogen, therefore the state of hydrogen can be described as neither liquid nor gas. Small disks, 0.8 mm in diameter and 0.1 mm thick, were punched from foils of the alloy to fill the specimen chamber. The specimens were pressurized to a preset pressure (8 or 10 GPa) at room temperature, and were subsequently heated to 800°C in hydrogen fluid. After the high pressure and high temperature treatments, the specimens were quenched at room temperature and depressurized.

High pressure and high temperature conditions were generated using a cubic anvil-type, high pressure apparatus installed in beamline BL14B1 at SPring-8, Japan.$^{14}$ Structural changes at high pressures and high temperatures were observed via an in situ X-ray diffraction measurement system. An incident white synchrotron radiation X-ray passed through a narrow gap (0.2 mm) between the pistons, which were used to generate high pressure and irradiated the specimen in a high pressure cell. Diffraction X-rays were measured by a germanium solid-state detector mounted on a goniometer in the energy dispersive mode. Lattice constants and lattice volumes of the specimens were calculated from the obtained powder X-ray diffraction profiles.

The high pressure cells used in this study consisted of a cubic pressure medium, resistant heater, hydrogen-sealing capsule made of NaCl, two pieces of internal hydrogen sources, and specimen which were put between the hydrogen sources.$^{15,16}$ The specimen was placed into the hydrogen-sealing capsule with internal hydrogen sources. These hydrogen sources expelled hydrogen at high pressure and high temperature, and then the specimen was immersed in hydrogen fluid to form its hydride.

3. Results and Discussion

Figure 1 shows the pressure dependence of the lattice constants and the lattice volume of Al$_3$Ti at room temperature. The Al$_3$Ti alloy is almost uniformly compressed within the experimental accuracy; structural phase transition is not observed until 10 GPa at room temperature. The obtained compression curve can be explained by the reported bulk modulus of Al$_3$Ti$^{17,18}$ and Birch-Murnaghan’s equation of state.

Figure 2 shows the series of X-ray diffraction profiles which are taken during the specimen is heated from 300–750°C at 10 GPa in hydrogen fluid. Figures 3(a), (b), and (c) show the temperature dependence of lattice constants $a$ and $c$, respectively.
and the lattice volume of Al$_3$Ti immersed. Due to thermal expansion, lattice constants $a$ and $c$ continuously increase below 620°C. However at 625°C, the lattice constants begin to increase discontinuously. These discontinuous changes terminate around 660°C, which corresponds to about a seven minute reaction. Above 660°C, the lattice constants increase continuously again. These discontinuous increases in lattice constants $a$ and $c$ are about 2 and 6 pm, respectively ($\Delta a/a \sim 0.5\%$, and $\Delta c/c \sim 0.7\%$; the $c$-axis expands slightly more than the $a$-axis). The calculated increase in the lattice volume is approximately 0.002 nm$^3$. Additionally, an anomalous expansion of Al$_3$Ti metal lattice is observed at 700°C and 8 GPa.

For comparison, we observed the temperature dependence of the lattice constants and volume of Al$_3$Ti alloy without high pressure hydrogen fluid at 10 GPa.
hydrogen fluid at 10 GPa. Figure 3(d) shows the temperature dependence of the lattice volume of the Al$_3$Ti alloy when the specimen is heated from 600 to 800°C. The lattice volume increases continuously over the entire temperature region without an anomalous lattice expansion. Therefore, the anomalous lattice expansion shown in Figs. 3(a), (b), and (c) are attributed to the hydrogenation reaction of Al$_3$Ti alloy, which forms Al$_3$TiH$_x$ (solid-solution phase).

The formed hydride phase, Al$_3$TiH$_x$, cannot be recovered at ambient conditions. Al$_3$TiH$_x$ is dehydrogenated during depressurization. The recovered specimen at ambient conditions is characterized as a single phase Al$_3$Ti alloy using a powder X-ray diffraction measurement.

If the amount of hydrogen-induced lattice expansion of Al$_3$Ti is assumed to be the same as that of the transition metals, then the calculated atomic ratio of hydrogen to metal (H/M) is about 0.1 (i.e., $x \approx 0.4$ for Al$_3$TiH$_x$). A typical volume change for transition metal hydrides is around 18% per hydrogen atom as calculated for one metal atom in the lattice. For Al$_3$Ti, the hydrogenation reaction is accompanied by a 2% increase in the lattice volume.

The hydrogen content of AlTi$_3$H$_x$ is low possibly due to the low affinity of aluminum for hydrogen. Solid-solution phase of pure FCC aluminum and hydrogen is not formed even just below the pressure-temperature conditions where aluminum trihydride AlH$_3$ is formed. Hydrogen atoms hardly occupy interstitial sites of Al$_3$Ti alloy on the analogy of pure aluminum, because the crystal structure of Al$_3$Ti is the superstructure derived from FCC aluminum.

4. Conclusions

Al$_3$Ti alloy is hydrogenated to form Al$_3$TiH$_x$ ($x \approx 0.4$) around 10 GPa and 600°C. The low hydrogen content is probably due to the low affinity of aluminum for hydrogen and the crystal structure of Al$_3$Ti, which is a superstructure derived from pure aluminum. Aluminum-based alloys with non-FCC structures are likely the next targets for exploring novel aluminum-based hydrides using high pressure techniques.

Acknowledgments

This work was supported by New Energy and Industrial Technology Development Organization (NEDO) under “Advanced Fundamental Research Project on Hydrogen Storage Materials”.

REFERENCES